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(54) 【発明の名称】 電解質膜及びその製造方法、並びに燃料電池及びその製造方法

## (57) 【要約】

【課題】 メタノールの透過 (クロスオーバー) をできるだけ抑制し、かつ高温 (約130℃以上) 環境下での使用にも耐える新規な電解質膜、及び該電解質膜を用いた燃料電池、特にメタノール直接型固体高分子燃料電池、並びにこれらの製造方法の提供。

【解決手段】 メタノールおよび水に対して実質的に膨潤しない多孔性基材の細孔にプロトン伝導性を有する第1及び第2のポリマーを充填した電解質膜であって、該第1のポリマーが前記基材の細孔内表面にその一端を結合させたポリマーである電解質膜により、上記課題を解決する。

## 【特許請求の範囲】

【請求項 1】 有機溶媒および水に耐膨潤性を有する多孔性基材の細孔内表面にその一端を結合させるように第 1 のポリマーを形成する工程、及び第 1 のポリマーと同じであっても異なってもよい第 2 のポリマーを前記基材の細孔内に充填させる工程を有する電解質膜の製造方法であって、前記第 1 及び第 2 のポリマーがプロトン伝導性を有する電解質膜の製造方法。

【請求項 2】 第 1 のポリマーが第 1 のモノマー由来であり、第 2 のポリマーが第 1 のモノマーと同じであっても異なってもよい第 2 のモノマー由来である請求項 1 記載の方法。

【請求項 3】 第 1 のポリマーの形成工程が、前記基材にエネルギーを照射する工程、及び該基材に第 1 のモノマーを接触させる工程を有し、第 1 のモノマーを接触させることにより、前記基材の細孔内表面にその一端を結合させるように第 1 のポリマーを形成する、請求項 1 又は請求項 2 記載の方法。

【請求項 4】 前記エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により前記基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第 1 のモノマーを接触させることにより、該反応開始点において前記基材と結合するように第 1 のポリマーを形成する、請求項 3 記載の方法。

【請求項 5】 第 1 のポリマーの形成工程が、カップリング剤により前記第 1 のポリマーの一端を前記基材に結合する請求項 1 又は請求項 2 記載の方法。

【請求項 6】 前記第 2 のポリマーの充填工程が、前記第 2 のモノマーを前記基材の細孔内に充填し、該充填した第 2 のモノマーを前記細孔内において重合させて第 2 のポリマーを得て、これにより細孔内を充填させる工程である請求項 2～請求項 5 のいずれか 1 項記載の方法。

【請求項 7】 前記多孔性基材は無機材料または耐熱性ポリマーから構成される請求項 1～請求項 6 のいずれか 1 項記載の方法。

【請求項 8】 前記無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料である請求項 7 記載の方法。

【請求項 9】 前記耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドである請求項 7 記載の方法。

【請求項 10】 前記電解質膜が燃料電池用電解質膜である請求項 1～請求項 9 のいずれか 1 項記載の方法。

【請求項 11】 前記電解質膜が直接型メタノール固体高分子燃料電池用電解質膜である請求項 1～請求項 9 のいずれか 1 項記載の方法。

【請求項 12】 メタノールおよび水に対して実質的に膨潤しない多孔性基材の細孔にプロトン伝導性を有するポリマーを充填したことを特徴とする電解質膜であって、該ポリマーが第 1 のプロトン伝導性ポリマー及び第

2 のプロトン伝導性ポリマーを有し、該第 1 のポリマーが前記基材の細孔内表面にその一端を結合させたポリマーであり、第 2 のポリマーが第 1 のポリマーと同じであっても異なってもよいポリマーである電解質膜。

【請求項 13】 第 1 のポリマーが第 1 のモノマー由来であり、第 2 のポリマーが第 1 のモノマーと同じであっても異なってもよい第 2 のモノマー由来である請求項 12 記載の電解質膜。

【請求項 14】 第 1 のポリマーが、前記基材にエネルギーを照射した後、該基材に第 1 のモノマーを接触させることによって得られる、請求項 12 又は請求項 13 記載の電解質膜。

【請求項 15】 前記エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により前記基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第 1 のモノマーを接触させることにより、該反応開始点において前記基材と結合するように第 1 のポリマーが得られる、請求項 14 記載の電解質膜。

【請求項 16】 第 1 のポリマーは、カップリング剤によりその一端を前記基材に結合する請求項 12 又は請求項 13 記載の方法。

【請求項 17】 前記第 2 のポリマーが、前記第 2 のモノマーを前記基材の細孔内に充填し、該充填した第 2 のモノマーを前記細孔内において重合させて得られる請求項 13～請求項 16 のいずれか 1 項記載の電解質膜。

【請求項 18】 前記多孔性基材は無機材料または耐熱性ポリマーから構成される請求項 12～請求項 17 のいずれか 1 項記載の電解質膜。

【請求項 19】 前記無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料である請求項 18 記載の電解質膜。

【請求項 20】 前記耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドである請求項 18 記載の電解質膜。

【請求項 21】 前記電解質膜が燃料電池用電解質膜である請求項 12～請求項 20 のいずれか 1 項記載の電解質膜。

【請求項 22】 前記電解質膜が直接型メタノール固体高分子燃料電池用電解質膜である請求項 12～請求項 20 のいずれか 1 項記載の電解質膜。

【請求項 23】 電解質膜を、カソード電極上またはカソード電極の触媒層上に形成した燃料電池であって、該電解質膜が請求項 12～22 のいずれか 1 項記載の電解質膜である燃料電池。

【請求項 24】 カソード極、アノード極、該両極に挟まれた電解質を有してなる燃料電池であって、該電解質は、メタノールおよび水に対して実質的に膨潤しない多孔性基材の細孔にプロトン伝導性を有するポリマーを充填したことを特徴とする電解質であり、該ポリマーが第

1のプロトン伝導性ポリマー及び第2のプロトン伝導性ポリマーを有し、該第1のポリマーが前記基材の細孔内表面にその一端を結合したポリマーであり、第2のポリマーが第1のポリマーと同じであっても異なってもよいポリマーである燃料電池。

【請求項25】 第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来である請求項24記載の燃料電池。

【請求項26】 第1のポリマーが、前記基材にエネルギーを照射した後、該基材に第1のモノマーを接触させることによって得られる、請求項24又は請求項25記載の燃料電池。

【請求項27】 前記エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により前記基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において前記基材と結合するように第1のポリマーが得られる、請求項25記載の燃料電池。

【請求項28】 第1のポリマーは、カップリング剤によりその一端を前記基材に結合する請求項24又は請求項25記載の方法。

【請求項29】 前記第2のポリマーが、前記第2のモノマーを前記基材の細孔内に充填し、該充填した第2のモノマーを前記細孔内において重合させて得られる請求項25～請求項28のいずれか1項記載の燃料電池。

【請求項30】 前記多孔性基材は無機材料または耐熱性ポリマーから構成される請求項24～請求項29のいずれか1項記載の燃料電池。

【請求項31】 前記無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料である請求項30記載の燃料電池。

【請求項32】 前記耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドである請求項30記載の燃料電池。

【請求項33】 前記燃料電池が、直接型メタノール固体高分子燃料電池である請求項24～請求項32のいずれか1項記載の燃料電池。

【請求項34】 ゾルを第1の極に塗布する工程、塗布したゾルを多孔性薄膜層にする工程、得られた多孔性薄膜層の細孔にプロトン伝導性ポリマーを充填して第1の電極上に電解質膜を形成する工程、該電解質膜上に第2の極を密着させる工程を有する燃料電池の製造方法であって、前記電解質膜を形成する工程において、前記プロトン伝導性ポリマーが第1及び第2のプロトン伝導性ポリマーを有し、該第1のポリマーの一端が前記細孔の表面に結合するように該第1のポリマーを形成する工程、及び第1のポリマーの形成後に第2のポリマーを充填する工程を有する燃料電池の製造方法。

【請求項35】 前記第1のポリマーと第2のポリマーとは同じであっても異なってもよい請求項34記載の方法。

【請求項36】 前記第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来である請求項34又は請求項35記載の方法。

【請求項37】 前記第1のポリマーの形成工程が、前記基材にエネルギーを照射した後、該基材に第1のモノマーを接触させることによって行われる請求項34～請求項36のいずれか1項記載の方法。

【請求項38】 前記エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により前記基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において前記基材と結合するように第1のポリマーが得られる、請求項37記載の方法。

【請求項39】 第1のポリマーの形成工程が、カップリング剤により前記第1のポリマーの一端を前記基材に結合する請求項34～請求項36のいずれか1項記載の方法。

【請求項40】 前記第2のポリマーが、前記第2のモノマーを前記基材の細孔内に充填し、該充填した第2のモノマーを前記細孔内において重合させることによって得られる請求項36～請求項39のいずれか1項記載の方法。

【請求項41】 前記多孔性基材は無機材料または耐熱性ポリマーから構成される請求項34～請求項40のいずれか1項記載の方法。

【請求項42】 前記無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料である請求項41記載の方法。

【請求項43】 前記耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドである請求項41記載の方法。

【請求項44】 前記第1の極が第1の支持体層及び第1の触媒層を有してなり、ゾル塗布工程において、前記ゾルを前記触媒層に塗布する請求項34～請求項43のいずれか1項記載の方法。

【請求項45】 前記第2の極が第2の支持体層及び第2の触媒層を有してなり、第2の極を密着させる工程において、前記電解質膜と前記第2の触媒層とを密着させる請求項34～請求項44のいずれか1項記載の方法。

【請求項46】 前記燃料電池が、直接型メタノール固体高分子燃料電池である請求項34～請求項45のいずれか1項記載の方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は一般に電解質膜に関

し、詳細には燃料電池用電解質膜、さらに詳細には直接型メタノール固体高分子型燃料電池用電解質膜に関する。また、本発明は、該電解質膜を有してなる燃料電池及びその製造方法に関する。

#### 【0002】

【従来の技術】地球的な環境保護の動きが活発化するにつれて、いわゆる温暖化ガスや $\text{NO}_x$ の排出防止が強く叫ばれている。これらのガスの総排出量を削減するために、自動車用の燃料電池システムの実用化が非常に有効と考えられている。

【0003】固体高分子型燃料電池（PEFC、Polymer Electrolyte Fuel Cell）は、低温動作、高出力密度、発電反応で水しか生成されないという優れた特徴を有している。なかでも、メタノール燃料のPEFCは、ガソリンと同様に液体燃料として供給が可能のため、電気自動車用動力として有望であると考えられている。

【0004】固体高分子型燃料電池は、改質器を用いてメタノールを水素主成分のガスに変換する改質型と、改質器を用いずにメタノールを直接使用する直接型（DMFC、Direct Methanol Polymer Fuel Cell）の二つのタイプに区分される。直接型燃料電池は、改質器が不要であるため、軽量化が可能であり、また頻繁な起動・停止に耐える、負荷変動応答性も大幅に改善できる、触媒被毒も問題にならないなどの大きな利点があり、その実用化が期待されている。

#### 【0005】

【発明が解決しようとする課題】しかしながら、DMFCの実用化にはいくつかの問題点が指摘されている。例えば、DMFCは電解質として固体高分子電解質を用いるが、在来PEFC用の電解質膜、例えばDu Pont社のNafion（登録商標）膜、Dow Chemical社のDow膜などを用いた場合には、メタノールが膜を透過してしまうため、触媒が消極し起電力が低下するという問題、及び触媒活性を上げるために温度を上げると130℃付近で融解（クリーピング）してしまうという問題の、大きな二つの問題が発生する。これらの問題を同時に解決する電解質膜は現存しないが、この問題を解決すれば電気自動車への応用が一気に進む可能性がある。

【0006】よって、本発明の目的は、メタノールの透過（クロスオーバー）をできるだけ抑制し、かつ高温（約130℃以上）環境下での使用にも耐える新規な電解質膜を実現することにある。また、本発明の目的は、上記電解質膜の製造方法を提供することにある。さらに、本発明の目的は、上記電解質膜を用いた新規なメタノール直接型固体高分子燃料電池を実現することにある。

#### 【0007】

【課題を解決するための手段】上記問題点を解決するため、本発明者らは、鋭意検討を重ねた結果、次のような知見を得た。即ち、一般にポリマーは高温で軟化する

が、熱分解する温度まではその性能を維持するという性質に着目し、耐熱性基材の細孔中に第1のポリマーを化学結合させて埋め込めば、高温下でも基材の骨格が膜の構造を維持するという知見を得た。

【0008】また、本発明者らは、第1のポリマーに加えて、第2のポリマーを充填させれば、メタノールの透過（クロスオーバー）を抑制しつつ、プロトン伝導性を高めることができるという知見を得た。さらに、プロトン伝導性は細孔中に埋め込んだポリマーにより確保するとともに、高温下における形状維持、膨潤抑制および耐熱性は多孔性基材のマトリクスにより達成することができるという知見を得た。

【0009】これらの知見から、本発明者らは、以下の発明を見出した。

<1> 有機溶媒および水に耐膨潤性を有する多孔性基材の細孔内表面にその一端を結合させるように第1のポリマーを形成する工程、及び第1のポリマーと同じであっても異なってもよい第2のポリマーを前記基材の細孔内に充填させる工程を有する電解質膜の製造方法であって、前記第1及び第2のポリマーがプロトン伝導性を有する電解質膜の製造方法。

【0010】<2> 上記<1>において、第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来であるのがよい。

<3> 上記<1>又は<2>において、第1のポリマーの形成工程が、基材にエネルギーを照射する工程、及び該基材に第1のモノマーを接触させる工程を有し、第1のモノマーを接触させることにより、基材の細孔内表面にその一端を結合させるように第1のポリマーを形成するのがよい。

【0011】<4> 上記<3>において、エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において基材と結合するように第1のポリマーを形成するのがよい。

<5> 上記<1>又は<2>において、第1のポリマーの形成工程が、カップリング剤により第1のポリマーの一端を基材に結合するのがよい。

【0012】<6> 上記<1>～<5>のいずれかにおいて、第2のポリマーの充填工程が、第2のモノマーを基材の細孔内に充填し、該充填した第2のモノマーを細孔内において重合させて第2のポリマーを得て、これにより細孔内を充填させる工程であるのがよい。

<7> 上記<1>～<6>のいずれかにおいて、多孔性基材は無機材料または耐熱性ポリマーから構成されるのがよい。

<8> 上記<7>において、無機材料は、セラミッ

ク、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料であるのがよい。

【0013】<9> 上記<7>において、耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドであるのがよい。

<10> 上記<1>～<9>のいずれかにおいて、電解質膜が燃料電池用電解質膜であるのがよい。

<11> 上記<1>～<9>のいずれかにおいて、電解質膜が直接型メタノール固体高分子燃料電池用電解質膜であるのがよい。

【0014】<12> メタノールおよび水に対して実質的に膨潤しない多孔性基材の細孔にプロトン伝導性を有するポリマーを充填したことを特徴とする電解質膜であって、該ポリマーが第1のプロトン伝導性ポリマー及び第2のプロトン伝導性ポリマーを有し、該第1のポリマーが前記基材の細孔内表面にその一端を結合させたポリマーであり、第2のポリマーが第1のポリマーと同じであっても異なってもよいポリマーである電解質膜。

【0015】<13> 上記<12>において、第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来であるのがよい。

<14> 上記<12>又は<13>において、第1のポリマーが、基材にエネルギーを照射した後、該基材に第1のモノマーを接触させることによって得られるのがよい。

【0016】<15> 上記<14>において、エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において前記基材と結合するように第1のポリマーが得られるのがよい。

<16> 上記<12>又は<13>において、第1のポリマーは、カップリング剤によりその一端を基材に結合するのがよい。

【0017】<17> 上記<12>～<16>のいずれかにおいて、第2のポリマーが、第2のモノマーを基材の細孔内に充填し、該充填した第2のモノマーを細孔内において重合させて得られるのがよい。

【0018】<18> 上記<12>～<17>のいずれかにおいて、多孔性基材は無機材料または耐熱性ポリマーから構成されるのがよい。

<19> 上記<18>において、無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料であるのがよい。

【0019】<20> 上記<18>において、耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドであるのがよい。

<21> 上記<12>～<20>のいずれかにおい

て、電解質膜が燃料電池用電解質膜であるのがよい。

<22> 上記<12>～<20>のいずれかにおいて、電解質膜が直接型メタノール固体高分子燃料電池用電解質膜であるのがよい。

【0020】<23> 電解質膜を、カソード電極上またはカソード電極の触媒層上に形成した燃料電池であって、該電解質膜が上記<12>～<22>のいずれかの電解質膜である燃料電池。

【0021】<24> カソード極、アノード極、該両極に挟まれた電解質を有してなる燃料電池であって、該電解質は、メタノールおよび水に対して実質的に膨潤しない多孔性基材の細孔にプロトン伝導性を有するポリマーを充填したことを特徴とする電解質であり、該ポリマーが第1のプロトン伝導性ポリマー及び第2のプロトン伝導性ポリマーを有し、該第1のポリマーが前記基材の細孔内表面にその一端を結合したポリマーであり、第2のポリマーが第1のポリマーと同じであっても異なってもよいポリマーである燃料電池。

【0022】<25> 上記<24>において、第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来であるのがよい。

<26> 上記<24>又は<25>において、第1のポリマーが、基材にエネルギーを照射した後、該基材に第1のモノマーを接触させることによって得られるのがよい。

【0023】<27> 上記<26>において、エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において基材と結合するように第1のポリマーが得られるのがよい。

<28> 上記<24>又は<25>において、第1のポリマーは、カップリング剤によりその一端を基材に結合するのがよい。

【0024】<29> 上記<24>～<28>のいずれかにおいて、第2のポリマーが、第2のモノマーを基材の細孔内に充填し、該充填した第2のモノマーを細孔内において重合させて得られるのがよい。

<30> 上記<24>～<29>のいずれかにおいて、多孔性基材は無機材料または耐熱性ポリマーから構成されるのがよい。

【0025】<31> 上記<30>において、無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料であるのがよい。

<32> 上記<30>において、耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドであるのがよい。

<33> 上記<24>～<32>のいずれかにおい

て、燃料電池が、直接型メタノール固体高分子燃料電池であるのがよい。

【0026】<34> ゾルを第1の極に塗布する工程、塗布したゾルを多孔性薄膜層にする工程、得られた多孔性薄膜層の細孔にプロトン伝導性ポリマーを充填して第1の電極上に電解質膜を形成する工程、該電解質膜上に第2の極を密着させる工程を有する燃料電池の製造方法であって、前記電解質膜を形成する工程において、前記プロトン伝導性ポリマーが第1及び第2のプロトン伝導性ポリマーを有し、該第1のポリマーの一端が前記細孔の表面に結合するように該第1のポリマーを形成する工程、及び第1のポリマーの形成後に第2のポリマーを充填する工程を有する燃料電池の製造方法。

【0027】<35> 上記<34>において、第1のポリマーと第2のポリマーとは同じであっても異なってもよい。

<36> 上記<34>又は<35>において、第1のポリマーが第1のモノマー由来であり、第2のポリマーが第1のモノマーと同じであっても異なってもよい第2のモノマー由来であるのがよい。

【0028】<37> 上記<34>～<36>のいずれかにおいて、第1のポリマーの形成工程が、基材にエネルギーを照射した後、該基材に第1のモノマーを接触させることによって行われるのがよい。

【0029】<38> 上記<37>において、エネルギーのエネルギー源が、プラズマ、紫外線、電子線、ガンマ線からなる群から選ばれ、該エネルギー源により基材を励起させて該基材の少なくとも細孔内表面に反応開始点を生成し、該反応開始点に第1のモノマーを接触させることにより、該反応開始点において基材と結合するように第1のポリマーが得られるのがよい。

<39> 上記<34>～<36>のいずれかにおいて、第1のポリマーの形成工程が、カップリング剤により第1のポリマーの一端を基材に結合するのがよい。

【0030】<40> 上記<34>～<39>のいずれかにおいて、第2のポリマーが、第2のモノマーを基材の細孔内に充填し、該充填した第2のモノマーを細孔内において重合させることによって得られるのがよい。

<41> 上記<34>～<40>のいずれかにおいて、多孔性基材は無機材料または耐熱性ポリマーから構成されるのがよい。

【0031】<42> 上記<41>において、無機材料は、セラミック、ガラスまたはアルミナのいずれか一つもしくはそれらの複合材料であるのがよい。

<43> 上記<41>において、耐熱性ポリマーがポリテトラフルオロエチレン又はポリイミドであるのがよい。

【0032】<44> 上記<34>～<43>のいずれかにおいて、第1の極が第1の支持体層及び第1の触媒層を有してなり、ゾル塗布工程において、前記ゾルを

前記触媒層に塗布するのがよい。

<45> 上記<34>～<44>のいずれかにおいて、第2の極が第2の支持体層及び第2の触媒層を有してなり、第2の極を密着させる工程において、前記電解質膜と前記第2の触媒層とを密着させるのがよい。

【0033】<46> 上記<34>～<45>のいずれかにおいて、燃料電池が、直接型メタノール固体高分子燃料電池であるのがよい。

【0034】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の電解質膜は、耐熱性を有し、メタノール等の有機溶媒および水に対して実質的に膨潤しない多孔性材料を基材として用いる。そのような性質を持つ材料として、無機材料ではガラス、又はアルミナもしくはシリカなどのセラミックス等がある。また、その他の材料ではポリテトラフルオロエチレン（例えばテフロン（登録商標））、ポリイミド等が挙げられる。これらの材料は、単独で用いても、2種以上を複合材料として用いてもよい。また、複合材料として用いる場合、その形態は2層以上が積層してなるものであってもよい。

【0035】本発明に用いることができる基材の空孔率は、好適には10%～95%であるのがよい。また、平均孔径は、0.001μm～100μmの範囲内にあることが望ましい。さらに、基材の厚さは100μm以下、好ましくは数μmのオーダーであるのがよい。

【0036】本発明の電解質膜は、多孔性材料からなる基材の表面、特に細孔内表面に、第1のポリマー、特にグラフト重合体を結合してなる。この第1のポリマーは、第1のモノマー由来であり、第1のモノマー及び第1のポリマーはイオン交換基を有する。この第1のポリマー、特にグラフト重合体がまず、基材の細孔内を満たす。第1のポリマーは、その一端が細孔内表面に結合するように形成されるため、細孔内に形成された該第1のポリマーは、容易に流出または溶出することがない。

【0037】なお、本明細書において、「イオン交換基」とは、例えば-SO<sub>3</sub>H基由来の-SO<sub>3</sub><sup>-</sup>など、プロトンを保持し且つ遊離しやすい基のことをいう。これらが第1のポリマーにペンダント状に存在し、かつ該ポリマーが細孔内を満たすことにより、プロトン伝導性が生じる。

【0038】第1のポリマーを、その一端を細孔内表面に結合するように形成するには、次のような方法がある。例えば、プラズマ、紫外線、電子線、ガンマ線等で基材を励起させて、該基材の少なくとも細孔内表面に反応開始点を生成させて、該反応開始点に第1のモノマーを接触させることにより、第1のポリマーを得る方法である。また、シランカブラー等の化学的方法により、第1のポリマーを細孔内表面に結合させることもできる。さらに、細孔中に第1のモノマーを充填し、その内部で重合反応を行わせて第1のポリマーを得る一般的な重合

法を用いた後に、得られた第1のポリマーを基材と、例えば上記シランカブラーなどを含むカップリング剤を用いて、化学結合させることもできる。

【0039】本発明において、以下に説明するプラズマグラフト重合法を用いるのが好ましい。即ち、第1のモノマーをプラズマグラフト重合反応させて、その一端が細孔表面に結合した第1のポリマーを得るのが好ましい。なお、プラズマグラフト重合は、以下に説明する液相法、及び周知の気相重合法を用いて行うことができる。

【0040】本発明の第1のモノマーとして使用可能なモノマーは、好適にはアクリルスルホン酸ナトリウム(SAS)、メタリルスルホン酸ナトリウム(SMS)、pスチレンスルホン酸ナトリウム(SSS)、アクリル酸(AA)などが挙げられる。しかしながら、本発明に使用可能なモノマーは、上記に限定されるものではなく、アリルアミン、アリルスルホン酸、アリルホスホン酸、メタリルスルホン酸、メタリルホスホン酸、ビニルスルホン酸、ビニルホスホン酸、スチレンスルホン酸、スチレンホスホン酸、アクリルアミドのスルホン酸またはホスホン酸誘導体、エチレンイミン、メタクリル酸など、構造中にビニル基およびスルホン酸、ホスホン酸などの強酸基、カルボキシル基などの弱酸基、1級、2級、3級、4級アミンのような強塩基、弱塩基を有するモノマーおよびそのエステルなどの誘導体であってもよい。なお、モノマーとしてナトリウム塩などの塩のタイプを用いた場合、ポリマーとした後に、それらの塩をプロトン型などにするのがよい。

【0041】また、これらのモノマーを1種のみ用いてホモポリマーを形成してもよく、2種以上用いてコポリマーを形成してもよい。即ち、基材の細孔内の表面にその一端が結合した第1のポリマーは、ホモポリマーであってもコポリマーであってもよい。

【0042】電解質膜のプロトン伝導性は、使用する第1のモノマー及び／又は後述する第2のモノマーの種類に依存して変化する。よって、高いプロトン伝導性を持つモノマー材料を用いることが望ましい。また、電解質のプロトン伝導性は、細孔内を満たすポリマーの重合度にも依存する。

【0043】なお、本発明においては、第1のポリマーと後述する第2のポリマーとを細孔内に形成及び／又は充填することにより、プロトン伝導性を付与している。したがって、第1のポリマー及び第2のポリマーとが双方共に高い重合度を有しているか、又はいずれか一方が高い重合度を有しているのがよい。特に、製造効率上、第2のポリマーが高い重合度を有するのがよい。もしくは、双方共に、相対的に高い重合度を有していないが、双方を併せることにより高いプロトン伝導性を有する程度の重合度をそれぞれが有するのがよい。

【0044】本発明の電解質膜の製造に使用可能なプラ

ズマグラフト重合法は、基材にプラズマを照射して、基材表面および細孔内表面に反応開始点を生成させた後に、好適には第1のモノマーを周知の液相重合の方法により接触させ、第1のモノマーを基材表面および細孔内部においてグラフト重合させる。

【0045】つぎに、本発明に使用可能なプラズマグラフト重合法について図面を参照しながら詳しく説明する。プラズマグラフト重合法の詳しい内容については、本発明の発明者らによる先行出願、特開平3-98632、特開平4-334531、特開平5-313433、特開平5-237352、特開平6-246141にも詳しく説明されている。

【0046】図1は、本発明の電解質膜に使用可能な多孔性基材1を示した部分断面斜視図である。多孔性基材1には、基材を貫通する細孔2が数多く開いている。

【0047】多孔性基材1に対し、圧力範囲が1mPaから120kPaとなるアルゴン、窒素、空気等のガスの存在下で、通常周波数10~50MHz、出力1~1000Wで、1~1000秒程度のプラズマ処理を行う。このときプラズマに曝された基材1の表面(細孔内表面も含む)には、反応開始点(図示せず)が発生する。

【0048】次に、イオン交換基を有する第1のモノマーを水に溶解させ、第1のモノマーの均一溶液を調製する。第1のモノマーの水溶液の濃度は、0.1~80重量%、好ましくは1~10重量%にすることが望ましい。なお、第1のモノマーの均一溶液は、該溶液が細孔内に浸入しやすいように、界面活性剤、例えばドデシルベンゼンスルホン酸などを有していてもよい。また、界面活性剤は、第2のモノマー溶液を用いる場合、該第2のモノマー溶液に含まれていてもよい。

【0049】プラズマ処理後の基材1は、上記第1のモノマーの水溶液と次のように処理するのがよい。即ち、アルゴンガス雰囲気下で、直接、第1のモノマー水溶液と接触させる。または、基材1を一旦空気中に取り出し、酸素と反応させてプラズマにより活性化した点をパーオキシド基に変換する。その後、パーオキシド基を有する基材1を第1のモノマー水溶液と接触させる。接触は、より具体的には、上記水溶液に、反応開始点が発生している多孔性基材1を浸漬することにより行う。なお、この工程は、アルゴンガス雰囲気下で直接行う場合、20℃~100℃、好ましくは30~60℃の温度で行うのがよく、パーオキシド基を発生させる場合、60℃~150℃、好ましくは80℃~120℃で行うのがよい。また、浸漬は、窒素ガス等の不活性ガスでバブリングしながら行うのがよい。浸漬する時間は1分から一日程度、好ましくは1時間~24時間であるのがよい。

【0050】次に、所定の時間経過した多孔性基材1を水溶液から引き上げ、トルエンまたはキシレン等の有機溶剤で洗浄し、乾燥させる。これは重合の過程で副次的

に生成されたホモポリマーなどを、有機溶剤で完全に洗い流し、基材細孔表面および内部のみにグラフト重合体を残すようにするためである。

【0051】図2は、基材1にモノマーがグラフト重合した状態を概念的に示した斜視図である。グラフト重合した第1のポリマー3が基材の表面だけではなく、細孔2の内部に形成されていることがわかる。

【0052】このようにして、その一端を多孔性基材の細孔表面に結合するように第1のポリマーが形成された基材が得られる。本発明において、次いで、得られた基材の細孔内に第2のポリマーを充填する。第2のポリマーはプロトン伝導性を有するポリマーであるのがよい。即ち、上述の第1のポリマーと同様に、イオン交換基を有するポリマーであれば、第1のポリマーと同じであっても異なってもよい。

【0053】第2のポリマーの充填方法は、第2のポリマーを直接細孔内に充填する方法、及びその後の処理により第2のポリマーとなる第2のモノマーを細孔内に充填した後、該細孔内で重合反応を行い第2のポリマーを得て、これにより第2のポリマーを細孔内に充填する方法などがある。

【0054】第2のモノマーを用いる場合、第2のモノマーは、第1のモノマーと同じであっても異なってもよい。即ち、上記で例示した第1のモノマーから1種又は2種以上を選択したものを用いることができる。好適な第2のモノマーとしては、第1のモノマーとして上述したものが挙げられ、且つこれに加えてビニルスルホン酸を挙げることができる。なお、第2のモノマーとして1種選択した場合、第2のポリマーはホモポリマーであり、第2のモノマーとして2種以上を選択した場合、第2のポリマーはコポリマーである。

【0055】第2のポリマーは、第1のポリマーと化学結合及び／又は物理結合しているのが好ましい。例えば、第2のポリマーが全て第1のポリマーと化学結合していてもよく、又は第2のポリマーが全て第1のポリマーと物理結合していてもよい。また、第2のポリマーの一部が第1のポリマーと化学結合しており、その他の第2のポリマーが第1のポリマーと物理結合していてもよい。なお、化学結合として、第1のポリマーと第2のポリマーとの結合が挙げられる。この結合は、例えば第1のポリマーに反応性基を保持させておき、該反応性基と第2のポリマー及び／又は第2のモノマーとが反応することなどにより、形成することができる。また、物理結合の状態として、例えば、第1及び第2のポリマー同士が絡み合う状態が挙げられる。

【0056】本発明において、第1及び第2のポリマーを併用することにより、メタノールの透過（クロスオーバー）を抑制しつつ、かつ細孔内に充填したポリマー全体が細孔内から溶出又は流出することなく、かつプロトン伝導性を高めることができる。特に、第1のポリマー

と第2のポリマーとが化学結合及び／又は物理結合することにより、細孔内に充填したポリマー全体が細孔内から溶出又は流出することがない。また、第1のポリマーの重合度が低い場合であっても、第2のポリマー、特に重合度が高い第2のポリマーが存在することにより、得られる電解質膜のプロトン伝導性を高めることができる。

【0057】以下、図3を用いて、第2のポリマーの充填方法を簡単に説明する。図3(a)は、第1のポリマーが形成された後の基材について、その細孔の断面を模式的に示した図である。図3(a)において、図2と同様な図番を用いており、基材1に細孔2が設けられており、第1のポリマー3が細孔2の表面にその一端が結合するように形成されている。

【0058】このように、第1のポリマーが形成されている基材の細孔に第2のモノマーを充填して、該細孔内で重合反応を行う。図3(b)は、重合反応により得られた第2のポリマー5が細孔内に充填していることを示している。上述のように、第2のポリマー5は、第1のポリマー3と化学結合及び／又は物理結合しており、第2のポリマー5も第1のポリマーと同様に、細孔外へ容易に流出又は溶出しなない。

【0059】本発明の電解質膜又は燃料電池及びそれらの製造方法において、第3のポリマー、第4のポリマー、...、第nのポリマー（即ち、nは3以上の整数）を用いることができる。第nのポリマーは、第2のポリマーと同様に、プロトン伝導性を高める作用を有していてもよい。また、第nのポリマーは、ポリマー全体が基材の細孔から流出又は溶出することを防ぐ作用を有していても、燃料電池に必要とされるその他の性質を有するように構成されていてもよい。

【0060】本発明の電解質膜は、燃料電池、特に直接型メタノール固体高分子燃料電池又は改質型メタノール固体高分子燃料電池を含むメタノール燃料電池に用いるのが好ましい。本発明の電解質膜は、直接型メタノール固体高分子燃料電池に用いるのが特に好ましい。

【0061】ここで、メタノール燃料電池の構成を、図4を参照しつつ、簡単に説明する。図4は、本発明の電解質膜を用いるメタノール燃料電池の一態様を示す概略図である。

【0062】メタノール燃料電池11は、カソード極13、アノード極15、及び該両極に挟まれた電解質17を有してなる。メタノール燃料電池は、図示しない改質器をアノード電極側に有し、改質型メタノール燃料電池としてもよい。

【0063】カソード極は、従来より公知の構成とすることができ、例えば電解質側から順に触媒層及び該触媒層を支持する支持体層を有してなることができる。また、アノード電極も、従来より公知の構成とすることができ、例えば電解質側から順に触媒層及び該触媒層を支



持する支持体層を有してなることができる。

【0064】さらに、本発明の電解質を有してなるメタノール燃料電池は、第1の極と電解質とを一体成形して成形体を得た後、第1の極とは異なる第2の極の触媒層と該電解質側とが密着するように、該成形体と第2の極とを密着させて得ることもできる。

【0065】第1の極がカソード極である場合を、図5を用いて説明する。図5は、本発明の電解質膜を用いるカソード極の一態様を示す概略図である。図5中、カソード極13は、支持体層19上に触媒層21を有してなる。該支持体層19は、ガス透過性、特に酸素ガス透過性、耐熱性及び電子導電性を有するものからなるのが好ましい。例えば多孔性カーボンであって電子導電性を有するものであるのがよい。

【0066】また、触媒層21は、カソード極に所望な、従来より公知の触媒を担持する層である。この触媒層21上に、図1に示すような、細孔2を有する多孔性薄膜23を形成する。多孔性薄膜の形成には、例えば種々のシリコンのアルコキシド、種々のアルミのアルコキシド、種々のチタンのアルコキシド、又は種々のジルコニウムのアルコキシドなど、種々のガラスまたはセラミックスとなるゾルを調製し、該ゾルを触媒層に塗布する。塗布法は、ディップコーティング、スピンコーティング、スプレーコーティングなど、従来より公知の方法を用いることができる。このようにして塗布されたゾルを乾燥、所望により加温して、多孔性薄膜を得る。なお、得られる多孔性薄膜は、シリカ、アルミナ（例えばγ-アルミナ）、チタニアもしくはジルコニア、又はこれらの混合体もしくは複合体の薄膜であるのがよい。

【0067】得られた多孔性薄膜の細孔内に、上述の第1のポリマー、例えばグラフト重合法、又はカップリング剤を用いる方法により、細孔内表面に該第1のポリマーの一端が結合するように、第1のポリマーを形成する。次いで、第2のポリマーを上述の方法により、細孔内に充填する。このようにして、カソード極と電解質とが一体成形することができる。このような一体成形体を用いることにより、薄膜化した電解質膜のハンドリングが容易になる。

【0068】この成形体とアノード極とを、アノード極の触媒層側と成形体の電解質側とが密着するように、密着成形してメタノール燃料電池を形成することができる。なお、上述において、カソード極と電解質とを一体成形する方法を述べたが、アノード極と電解質とを一体成形することも、当業者であれば、上述から容易に想到することができるであろう。

【0069】

【実施例】本発明を実施例に基づき、さらに詳しく説明するが、本発明は本実施例に限定されるものではない。

（実施例1）基材として多孔性PTFE膜（商標テフロン、日東電工製、平膜、厚さ70μm、細孔径50n

m）を用いた。当該基材を洗浄し、以下の条件でプラズマ照射を行った。

【0070】高周波出力：30W；

プラズマ照射時間：60秒間；

雰囲気：アルゴンガス；

圧力：10Pa。

【0071】プラズマ照射後の基材を、凍結脱気した第1のモノマー溶液に浸漬し、グラフト重合を行った。グラフト重合条件を以下に示す。

【0072】モノマー：アクリル酸（AA）；

モノマー濃度：10重量%；

溶媒：水；

温度：約60℃；

時間：10～24時間；及び

添加剤：界面活性剤（ドデシルベンゼンスルホン酸ナトリウム）。

【0073】多孔性基材を溶液から引き上げ、水中で洗浄した後、乾燥させて第1のポリマーを形成した膜A-1を得た。乾燥後に膜A-1の質量を測定し、重合前の質量と比較してグラフト重合量を計算した。グラフト重合量は0.7mg/cm<sup>2</sup>であった。ちなみに、重合後の膜厚は約90μmであった。

【0074】こうして得られた膜A-1をFT-IR（Mapping法）測定したところ、カルボキシル基の1740cm<sup>-1</sup>のピークが膜の内部でも存在することが確認され、膜の内部にもポリマーが形成されていることが判明した。

【0075】＜第2のポリマーの充填＞次いで、第2のポリマーの充填を行った。第2のモノマーとして第1のポリマーと同様にアクリル酸（AA）を用いた。第2のモノマー98.9重量部、架橋剤としてジビニルベンゼン0.1重量部、及び水溶性アゾ系重合開始剤1.0重量部からなる第2のモノマー溶液を調製した。この第2のポリマー溶液に、上記で得られた膜A-1を浸漬した。

【0076】浸漬後、可視光を6分間照射し、熱重合反応を細孔内部で行わせた。その後、得られた膜を超音波中で水洗浄し、乾燥して第1及び第2のポリマーを充填させた膜A-2を得た。なお、第2のポリマーの充填前後の重量の差から、重合量は7.0mg/cm<sup>2</sup>であることがわかった。

【0077】（実施例2）第2のモノマーとしてアクリル酸（AA）：ビニルスルホン酸＝2：1の混合物を用い、かつビニルスルホン酸を溶解するために若干量の水を用いた以外、実施例1と同様の方法により、膜A-3を得た。

【0078】（参照例1）実施例1の膜A-1と同様に、第1のポリマーのみを充填した膜A-4を得た。但し、膜A-4の重合量は、3.0mg/cm<sup>2</sup>であった。

【0079】＜プロトン伝導性測定＞得られた膜A-2～A-4について、そのプロトン伝導性を測定した。測定に際し、まず、膜を水中で膨潤させ、その後ステンレス箔電極に挟んでプロトン伝導性測定用試料を作製した。これらの試料について、ヒューレット・パッカード社製HP4192Aによりインピーダンス測定を行った。得られた結果を以下に示す。

【0080】膜A-4（参照例1）： $0.04 \times 10^{-2} \text{ S/cm}$ ；

膜A-2（実施例1）： $0.10 \times 10^{-2} \text{ S/cm}$ ； 及び

膜A-3（実施例2）： $0.62 \times 10^{-2} \text{ S/cm}$ 。

【0081】このように、第2のポリマーを充填することにより、高いプロトン伝導性を得ることができた。なお、膜A-2及びA-3はいずれも、所望の耐熱性及びメタノール阻止性能を有していた。即ち、本実施例の電解質膜A-2及びA-3は、メタノールの低透過性、耐熱性、及び高いプロトン伝導性を有することがわかった。

【0082】

【発明の効果】本発明により、メタノールの透過（クロスオーバー）をできるだけ抑制し、かつ高温（約130

℃以上）環境下での使用にも耐える新規な電解質膜を提供することができる。また、本発明により、上記効果の他に、又は上記効果に加えて、上記電解質膜を製造する方法を提供することができる。さらに、本発明により、上記効果の他に、又は上記効果に加えて、上記電解質膜を用いた新規なメタノール直接型固体高分子燃料電池を提供することができる。

【図面の簡単な説明】

【図1】 本発明に用いる多孔性基材の模式図である。

【図2】 本発明に用いる多孔性基材の細孔に第1のモノマーを形成したことを示す模式図である。

【図3】 本発明の第2のポリマーを充填する模式図である。

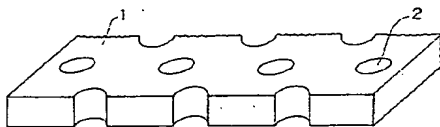
【図4】 本発明の電解質膜を用いるメタノール燃料電池の一態様を示す概略図である。

【図5】 本発明の電解質膜を用いるカソード電極の一態様を示す概略図である。

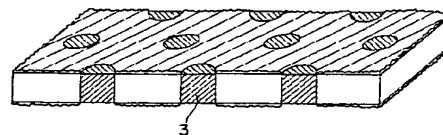
【符号の説明】

- 1 多孔性基材、2 細孔、3 第1のポリマー、5 第2のポリマー、11 メタノール燃料電池、13 カソード極、15 アノード極、17 電解質、19 支持体層、21 触媒層、23 多孔性薄膜

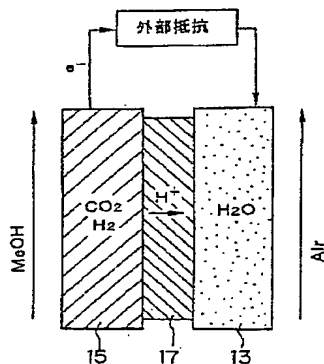
【図1】



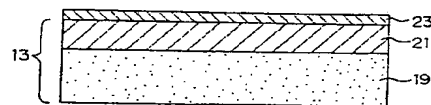
【図2】



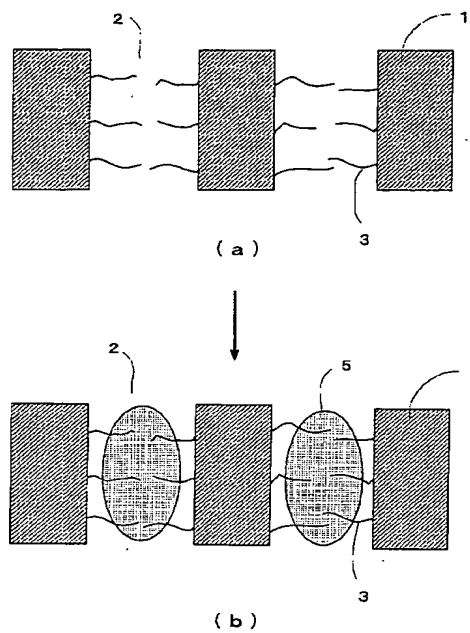
【図4】



【図5】



【図3】



フロントページの続き

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(54) ELECTROLYTE FILM AND ITS MANUFACTURING METHOD, AND FUEL CELL AND ITS  
MANUFACTURING METHOD

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a new electrolyte film, in which permeation of methanol (cross-over) is restrained as much as possible and which is also durable under an environment of higher temperature (not lower than about 130° C), and a fuel cell using the electrolyte film, especially methanol direct type solid polymer fuel cell, as well as to provide its manufacturing method.

SOLUTION: This electrolyte film, in which the first and the second polymers having a protonic conductivity are filled in fine pores of porous base material, which substantially does not swell with respect to methanol and water, and the electrolyte film where one end of the first polymer is made to be bonded to an inner surface of fine pores of the base material is used.

## LEGAL STATUS

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of an electrolyte membrane that are the manufacture approach of an electrolyte membrane of having the process which makes it filled up with the 2nd polymer which may differ even if the same as the process which forms the 1st polymer, and the 1st polymer so that the end may be combined with the pore internal surface of a porous base material which has bloating tendency-proof in an organic solvent and water in the pore of said base material, and said 1st and 2nd polymers have proton conductivity.

[Claim 2] The approach according to claim 1 of the 1st polymer being the 1st monomer origin and being the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[Claim 3] The approach according to claim 1 or 2 the formation process of the 1st polymer forms the 1st polymer so that the end may be combined with the pore internal surface of said base material by having the process which irradiates energy at said base material, and the process which contacts the 1st monomer to this base material, and contacting the 1st monomer.

[Claim 4] The approach according to claim 3 of forming the 1st polymer so that the energy source of said energy may be chosen from the group which consists of the plasma, ultraviolet rays, an electron ray, and a gamma ray, may excite said base material by this energy source and may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

[Claim 5] The approach according to claim 1 or 2 the formation process of the 1st polymer combines the end of said 1st polymer with said base material by the coupling agent.

[Claim 6] The approach of claim 2 - claim 5 given in any 1 term the restoration process of said 2nd polymer is a process which it is filled up with said 2nd monomer in the pore of said base material, and the polymerization of the 2nd monomer with which it was this filled up is carried out into said pore, and the 2nd polymer is obtained, and is made by this to fill up with the inside of pore.

[Claim 7] Said porous base material is the approach of claim 1 which consists of an inorganic material or a heat-resistant polymer - claim 6 given in any 1 term.

[Claim 8] Said inorganic material is the approach according to claim 7 of being any one or those composite material of a ceramic, glass, or an alumina.

[Claim 9] The approach according to claim 7 said heat-resistant polymer is polytetrafluoroethylene or polyimide.

[Claim 10] The approach of claim 1 - claim 9 given in any 1 term said electrolyte membrane is an electrolyte membrane for fuel cells.

[Claim 11] The approach of claim 1 - claim 9 given in any 1 term said electrolyte membrane is an electrolyte membrane for direct mold methanol solid-state macromolecule fuel cells.

[Claim 12] The electrolyte membrane which it is the electrolyte membrane characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity, and this polymer has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer is a polymer which combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[Claim 13] The electrolyte membrane according to claim 12 which the 1st polymer is the 1st monomer origin and is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[Claim 14] The electrolyte membrane according to claim 12 or 13 obtained by contacting the 1st monomer

to this base material after the 1st polymer irradiates energy at said base material.

[Claim 15] The electrolyte membrane according to claim 14 with which the 1st polymer is obtained so that the energy source of said energy may be chosen from the group which consists of the plasma, ultraviolet rays, an electron ray, and a gamma ray, may excite said base material by this energy source and may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

[Claim 16] The 1st polymer is the approach according to claim 12 or 13 of combining the end with said base material by the coupling agent.

[Claim 17] The electrolyte membrane of claim 13 – claim 16 given in any 1 term with which it is filled up with said 2nd monomer in the pore of said base material, and said 2nd polymer carries out the polymerization of the 2nd monomer with which it was this filled up into said pore, and is obtained.

[Claim 18] Said porous base material is the electrolyte membrane of claim 12 which consists of an inorganic material or a heat-resistant polymer – claim 17 given in any 1 term.

[Claim 19] Said inorganic material is an electrolyte membrane according to claim 18 which is any one or those composite material of a ceramic, glass, or an alumina.

[Claim 20] The electrolyte membrane according to claim 18 said whose heat-resistant polymer is polytetrafluoroethylene or polyimide.

[Claim 21] The electrolyte membrane of claim 12 said whose electrolyte membrane is an electrolyte membrane for fuel cells – claim 20 given in any 1 term.

[Claim 22] The electrolyte membrane of claim 12 said whose electrolyte membrane is an electrolyte membrane for direct mold methanol solid-state macromolecule fuel cells – claim 20 given in any 1 term.

[Claim 23] The fuel cell this whose electrolyte membrane it is the fuel cell in which the electrolyte membrane was formed on the cathode electrode or the catalyst bed of a cathode electrode, and is an electrolyte membrane of claim 12–22 given in any 1 term.

[Claim 24] It is the fuel cell which comes to have the electrolyte inserted into a cathode pole, an anode pole, and these two poles. This electrolyte It is the electrolyte characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity. The fuel cell which this polymer is a polymer to which it has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[Claim 25] The fuel cell according to claim 24 which the 1st polymer is the 1st monomer origin and is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[Claim 26] The fuel cell according to claim 24 or 25 obtained by contacting the 1st monomer to this base material after the 1st polymer irradiates energy at said base material.

[Claim 27] The fuel cell according to claim 25 with which the 1st polymer is obtained so that the energy source of said energy may be chosen from the group which consists of the plasma, ultraviolet rays, an electron ray, and a gamma ray, may excite said base material by this energy source and may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

[Claim 28] The 1st polymer is the approach according to claim 24 or 25 of combining the end with said base material by the coupling agent.

[Claim 29] The fuel cell of claim 25 – claim 28 given in any 1 term with which it is filled up with said 2nd monomer in the pore of said base material, and said 2nd polymer carries out the polymerization of the 2nd monomer with which it was this filled up into said pore, and is obtained.

[Claim 30] Said porous base material is the fuel cell of claim 24 which consists of an inorganic material or a heat-resistant polymer – claim 29 given in any 1 term.

[Claim 31] Said inorganic material is a fuel cell according to claim 30 which is any one or those composite material of a ceramic, glass, or an alumina.

[Claim 32] The fuel cell according to claim 30 said whose heat-resistant polymer is polytetrafluoroethylene or polyimide.

[Claim 33] The fuel cell of claim 24 said whose fuel cell is a direct mold methanol solid-state macromolecule fuel cell – claim 32 given in any 1 term.

[Claim 34] The process which applies a sol to the 1st pole, the process which uses the applied sol as a porous thin film layer, The process which fills up the pore of the obtained porous thin film layer with a proton conductivity polymer, and forms an electrolyte membrane on the 1st electrode, In the process

which is the manufacture approach of a fuel cell of having the process at which the 2nd pole is stuck, and forms said electrolyte membrane on said electrolyte membrane. Said proton conductivity polymer has the 1st and 2nd proton conductivity polymers. The manufacture approach of a fuel cell of having the process which forms this 1st polymer so that the end of this 1st polymer may combine with the front face of said pore, and the process filled up with the 2nd polymer after formation of the 1st polymer.

[Claim 35] Said the 1st polymer and 2nd polymer are the approach according to claim 34 which may be the same or may differ.

[Claim 36] The approach according to claim 34 or 35 of said 1st polymer being the 1st monomer origin, and being the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[Claim 37] The approach of claim 34 – claim 36 given in any 1 term performed by contacting the 1st monomer to this base material after the formation process of said 1st polymer irradiates energy at said base material.

[Claim 38] The approach according to claim 37 by which the 1st polymer is obtained so that the energy source of said energy may be chosen from the group which consists of the plasma, ultraviolet rays, an electron ray, and a gamma ray, may excite said base material by this energy source and may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

[Claim 39] The approach of claim 34 – claim 36 given in any 1 term the formation process of the 1st polymer combines the end of said 1st polymer with said base material by the coupling agent.

[Claim 40] The approach of claim 36 which said 2nd polymer is filled up with said 2nd monomer in the pore of said base material, and is obtained by carrying out the polymerization of the 2nd monomer with which it was this filled up into said pore – claim 39 given in any 1 term.

[Claim 41] Said porous base material is the approach of claim 34 which consists of an inorganic material or a heat-resistant polymer – claim 40 given in any 1 term.

[Claim 42] Said inorganic material is the approach according to claim 41 of being any one or those composite material of a ceramic, glass, or an alumina.

[Claim 43] The approach according to claim 41 said heat-resistant polymer is polytetrafluoroethylene or polyimide.

[Claim 44] The approach of claim 34 – claim 43 given in any 1 term said 1st pole comes to have the 1st base material layer and 1st catalyst bed, and applies said sol to said catalyst bed in a sol spreading process.

[Claim 45] The approach of claim 34 to which said electrolyte membrane and said 2nd catalyst bed are stuck in the process at which said 2nd pole comes to have the 2nd base material layer and 2nd catalyst bed, and sticks the 2nd pole – claim 44 given in any 1 term.

[Claim 46] The approach of claim 34 – claim 45 given in any 1 term said fuel cell is a direct mold methanol solid-state macromolecule fuel cell.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Generally, about an electrolyte membrane, it is related with a detail at the electrolyte membrane for fuel cells, and a pan, and this invention relates to a detail at the electrolyte membrane for direct mold methanol polymer electrolyte fuel cells. Moreover, this invention relates to the fuel cell which comes to have this electrolyte membrane, and its manufacture approach.

[0002]

[Description of the Prior Art] The so-called blowdown prevention of greenhouse gases and NO<sub>x</sub> is strongly cried for as the movement toward terrestrial environmental protection activates. In order to reduce the total emission of these gas, utilization of the fuel cell system for automobiles is considered to be very effective.

[0003] The polymer electrolyte fuel cell (PEFC, Polymer Electrolyte Fuel Cell) has the outstanding description that only water is generated at low-temperature actuation, high power density, and a generation-of-electrical-energy reaction. In as well as [ a gasoline ], since it can supply as liquid fuel, it is thought that PEFC of a methanol fuel is promising as power for electric vehicles.

[0004] A polymer electrolyte fuel cell is classified into two types, the refining mold which changes a methanol into the gas of a hydrogen principal component using a refining machine, and the direct mold (DMFC, Direct Methanol Polymer Fuel Cell) which uses a methanol directly, without using a refining machine. A direct mold fuel cell has the big advantage of that the load-effect responsibility which can be equal to frequent starting and halt possible [ lightweight-izing ] is also substantially improvable since the refining machine is unnecessary, catalyst poisoning not becoming a problem, either, and the utilization is expected.

[0005]

[Problem(s) to be Solved by the Invention] However, some troubles are pointed out to utilization of DMFC. For example, although DMFC uses a solid-state polyelectrolyte as an electrolyte When the electrolyte membrane for ordinary PEFC, for example, the Nafion (trademark) film of Du Pont, the Dow film of Dow Chemical, etc. are used Two big problems of the problem of dissolving near 130 degree C if temperature is raised in order to raise the problem that a catalyst carries out depolarization and electromotive force declines in order that a methanol may penetrate the film, and catalytic activity (creeping) occur. Although the electrolyte membrane which solves these problems simultaneously is not existing, if this problem is solved, the application to an electric vehicle may progress at a stretch.

[0006] Therefore, the object of this invention is to realize the new electrolyte membrane which controls transparency (crossover) of a methanol as much as possible, and is equal also to the activity under an elevated-temperature (about 130 degrees C or more) environment. Moreover, the object of this invention is to offer the manufacture approach of the above-mentioned electrolyte membrane. Furthermore, the object of this invention is to realize the new methanol direct mold solid-state macromolecule fuel cell which used the above-mentioned electrolyte membrane.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, this invention persons acquired the following knowledge, as a result of repeating examination wholeheartedly. That is, generally, although the polymer was softened at the elevated temperature, when the temperature to pyrolyze carried out the chemical bond of the 1st polymer and embedded it into the pore of a heat-resistant base material paying attention to the property to maintain the engine performance, the knowledge that the frame of a base material maintained membranous structure also under an elevated temperature was acquired.



[0008] Moreover, this invention persons acquired the knowledge that proton conductivity could be raised, controlling transparency (crossover) of a methanol, when you made it filled up in the 2nd polymer in addition to the 1st polymer. Furthermore, while securing proton conductivity by the polymer embedded into pore, the configuration maintenance under an elevated temperature, swelling control, and thermal resistance acquired the knowledge that the matrix of a porous base material could attain.

[0009] From these knowledge, this invention persons found out the following invention.

<1> The manufacture approach of an electrolyte membrane that are the manufacture approach of an electrolyte membrane of having the process which makes it filled up with the 2nd polymer which may differ even if the same as the process which forms the 1st polymer, and the 1st polymer so that the end may be combined with the pore internal surface of a porous base material which has bloating tendency-proof in an organic solvent and water in the pore of said base material, and said 1st and 2nd polymers have proton conductivity.

[0010] <2> In the above <1>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<3> In the above <1> or <2>, it is good to form the 1st polymer so that the end may be combined with the pore internal surface of a base material by having the process to which the formation process of the 1st polymer irradiates energy at a base material, and the process which contacts the 1st monomer to this base material, and contacting the 1st monomer.

[0011] <4> In the above <3>, it is good to form the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<5> In the above <1> or <2>, it is good for the formation process of the 1st polymer to combine the end of the 1st polymer with a base material by the coupling agent.

[0012] <6> In either of above-mentioned <1>- <5>, it is good that it is the process which the polymerization of the 2nd monomer with which the restoration process of the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material is carried out into pore, and the 2nd polymer is obtained, and is made by this to fill up with the inside of pore.

<7> In either of above-mentioned <1>- <6>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

<8> As for an inorganic material, in the above <7>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

[0013] <9> In the above <7>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<10> In either of above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

<11> In either of above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte membrane for direct mold methanol solid-state macromolecule fuel cells.

[0014] <12> It is the electrolyte membrane characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity. The electrolyte membrane which this polymer has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer is a polymer which combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[0015] <13> In the above <12>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<14> In the above <12> or <13>, after the 1st polymer irradiates energy at a base material, it is good to be obtained by contacting the 1st monomer to this base material.

[0016] <15> In the above <14>, it is good to obtain the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<16> In the above <12> or <13>, the 1st polymer is good to combine the end with a base material by the coupling agent.

[0017] <17> In either of above-mentioned <12>- <16>, it is good to carry out the polymerization of the 2nd

monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore, and to be obtained.

[0018] <18> In either of above-mentioned <12>- <17>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

<19> As for an inorganic material, in the above <18>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

[0019] <20> In the above <18>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<21> In either of above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

<22> In either of above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for direct mold methanol solid-state macromolecule fuel cells.

[0020] <23> Fuel cell this whose electrolyte membrane it is the fuel cell in which the electrolyte membrane was formed on the cathode electrode or the catalyst bed of a cathode electrode, and is one electrolyte membrane of above-mentioned <12>- <22>.

[0021] <24> It is the fuel cell which comes to have the electrolyte inserted into a cathode pole, an anode pole, and these two poles. This electrolyte It is the electrolyte characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity. The fuel cell which this polymer is a polymer to which it has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[0022] <25> In the above <24>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<26> In the above <24> or <25>, after the 1st polymer irradiates energy at a base material, it is good to be obtained by contacting the 1st monomer to this base material.

[0023] <27> In the above <26>, it is good to obtain the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<28> In the above <24> or <25>, the 1st polymer is good to combine the end with a base material by the coupling agent.

[0024] <29> In either of above-mentioned <24>- <28>, it is good to carry out the polymerization of the 2nd monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore, and to be obtained.

<30> In either of above-mentioned <24>- <29>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

[0025] <31> As for an inorganic material, in the above <30>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

<32> In the above <30>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<33> In either of above-mentioned <24>- <32>, it is good that a fuel cell is a direct mold methanol solid-state macromolecule fuel cell.

[0026] <34> The process which applies a sol to the 1st pole, the process which uses the applied sol as a porous thin film layer, The process which fills up the pore of the obtained porous thin film layer with a proton conductivity polymer, and forms an electrolyte membrane on the 1st electrode, In the process which is the manufacture approach of a fuel cell of having the process at which the 2nd pole is stuck, and forms said electrolyte membrane on this electrolyte membrane Said proton conductivity polymer has the 1st and 2nd proton conductivity polymers. The manufacture approach of a fuel cell of having the process which forms this 1st polymer so that the end of this 1st polymer may combine with the front face of said pore, and the process filled up with the 2nd polymer after formation of the 1st polymer.

[0027] <35> In the above <34>, the 1st polymer and 2nd polymer may be the same, or may differ from each other.

<36> In the above <34> or <35>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[0028] <37> In either of above-mentioned <34>- <36>, after the formation process of the 1st polymer irradiates energy at a base material, it is good to be carried out by contacting the 1st monomer to this

base material.

[0029] <38> In the above <37>, it is good to obtain the 1st polymer so that it be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<39> In either of above-mentioned <34>- <36>, it is good for the formation process of the 1st polymer to combine the end of the 1st polymer with a base material by the coupling agent.

[0030] <40> In either of above-mentioned <34>- <39>, it is good to be obtained by carrying out the polymerization of the 2nd monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore.

<41> In either of above-mentioned <34>- <40>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

[0031] <42> As for an inorganic material, in the above <41>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

<43> In the above <41>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

[0032] <44> In either of above-mentioned <34>- <43>, it is good for the 1st pole to come to have the 1st base material layer and 1st catalyst bed, and to apply said sol to said catalyst bed in a sol spreading process.

<45> In either of above-mentioned <34>- <44>, it is good to stick said electrolyte membrane and said 2nd catalyst bed in the process at which the 2nd pole comes to have the 2nd base material layer and 2nd catalyst bed, and sticks the 2nd pole.

[0033] <46> In either of above-mentioned <34>- <45>, it is good that a fuel cell is a direct mold methanol solid-state macromolecule fuel cell.

[0034]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The electrolyte membrane of this invention has thermal resistance, and the foam which is not substantially swollen to an organic solvent and water, such as a methanol, is used for it as a base material. As an ingredient with such a property, there is ceramics, such as glass, an alumina, or a silica, etc. with an inorganic material. Moreover, with other ingredients, polytetrafluoroethylene (for example, Teflon (trademark)), polyimide, etc. are mentioned. These ingredients may be used independently or two or more sorts may be used for them as a composite material. Moreover, when using as a composite material, more than two-layer may come to carry out the laminating of the gestalt.

[0035] As for the void content of the base material which can be used for this invention, it is suitably good that it is 10% - 95%. Moreover, as for an average aperture, it is desirable that it is within the limits of 0.001 micrometers - 100 micrometers. Furthermore, as for the thickness of a base material, it is preferably good that it is [ 100 micrometers or less ] several micrometers order.

[0036] The electrolyte membrane of this invention comes to combine the 1st polymer, especially a graft polymer with the front face, especially pore internal surface of the base material which consists of foam. This 1st polymer is the 1st monomer origin, and the 1st monomer and 1st polymer have an ion exchange group. This 1st polymer, especially a graft polymer fill the inside of the pore of a base material first. Since the 1st polymer is formed so that the end may combine with a pore internal surface, this 1st polymer formed in pore is not flowed out or eluted easily.

[0037] In addition, in this description, an "ion exchange group" means the radical which  $-SO_3^-$  or for example, the  $-SO_3H$  set origin etc. holds a proton, and is easy to separate. When these exist in the 1st polymer in the shape of a pendant and this polymer fills the inside of pore, proton conductivity arises.

[0038] In order to form the 1st polymer so that the end may be combined with a pore internal surface, there are the following approaches. For example, a base material is excited by the plasma, ultraviolet rays, the electron ray, a gamma ray, etc., and it is the approach of obtaining the 1st polymer, by [ of this base material ] making a pore internal surface generate a reaction start point at least, and contacting the 1st monomer to this reaction start point. Moreover, the 1st polymer can also be combined with a pore internal surface by the chemical approach of a silane coupler etc. Furthermore, it is filled up with the 1st monomer into pore, and after using the general polymerization method for making a polymerization reaction perform in the interior, and obtaining the 1st polymer, the chemical bond of the 1st obtained polymer can be carried out to a base material using the coupling agent containing for example, the above-mentioned silane coupler etc.

[0039] In this invention, it is desirable to use the plasma graft polymerization method explained below. That

is, it is desirable to obtain the 1st polymer which was made to carry out the plasma graft polymerization reaction of the 1st monomer, and then combined with the pore front face. In addition, plasma graft polymerization can be performed using the liquid phase process explained below and a well-known vapor-phase-polymerization method.

[0040] As for a monomer usable as the 1st monomer of this invention, acrylic sulfonic-acid sodium (SAS), sodium methallylsulfonate (SMS), p styrene sulfonic-acid sodium (SSS), an acrylic acid (AA), etc. are mentioned suitably. However, a monomer usable to this invention is not limited above but allylamine, an allyl compound sulfonic acid, Allyl compound phosphonic acid, a metallyl sulfonic acid, metallyl phosphonic acid, a vinyl sulfonic acid, Vinyl phosphonic acid, a styrene sulfonic acid, styrene phosphonic acid, the sulfonic acid of acrylamide, or a phosphonic acid derivative, Ethyleneimine, methacrylic acids, etc. may be derivatives, such as a monomer which has weak acid radicals, such as strong acid radicals, such as a vinyl group and a sulfonic acid, and phosphonic acid, and a carboxyl group, the 1st class, the 2nd class, the 3rd class, a strong base like the 4th class amine, and a weak base in structure, and its ester. In addition, when the type of salts, such as sodium salt, is used as a monomer, after considering as a polymer, it is good to use those salts as a proton mold etc.

[0041] Moreover, one sort of homopolymers may be formed using these monomers, two or more sorts may be used and a copolymer may be formed. That is, the 1st polymer which the end combined with the front face in the pore of a base material may be a homopolymer, or may be a copolymer.

[0042] The proton conductivity of an electrolyte membrane changes depending on the class of the 1st monomer to be used and/or the 2nd monomer mentioned later. Therefore, it is desirable to use a monomer ingredient with high proton conductivity. Moreover, it depends for electrolytic proton conductivity also on the polymerization degree of the polymer which fills the inside of pore.

[0043] In addition, in this invention, proton conductivity is given by being formed and/or filled up with the 1st polymer and the 2nd polymer mentioned later in pore. Therefore, it is good for the 1st polymer and 2nd polymer to have polymerization degree with high both sides, or to crawl, and for a gap or one side to have high polymerization degree. It is good for the 2nd polymer to have high polymerization degree on manufacture effectiveness especially. Or although both sides do not have high polymerization degree relatively, it is good by combining both sides for each to have the polymerization degree of extent which has high proton conductivity.

[0044] After a plasma graft polymerization method usable to manufacture of the electrolyte membrane of this invention irradiates the plasma at a base material and makes a base material front face and a pore internal surface generate a reaction start point, it is suitably contacted by the approach of the liquid phase polymerization common knowledge of the 1st monomer, and carries out the graft polymerization of the 1st monomer in the interior of a base material front face and pore.

[0045] It explains in detail, referring to a drawing about an usable plasma graft polymerization method to this invention next. The detailed content of the plasma graft polymerization method is explained also to the precedence application by the artificers of this invention, JP,3-98632,A, JP,4-334531,A, JP,5-31343,A, JP,5-237352,A, and JP,6-246141,A in detail.

[0046] Drawing 1 is the partial cross-section perspective view having shown the usable porous base material 1 in the electrolyte membrane of this invention. To the porous base material 1, the pore 2 which penetrates a base material is opening many.

[0047] The frequency of 10-50MHz is performed to the porous base material 1 under existence of gas, such as an argon with which a pressure range serves as 120kPa(s) from 1mPa, nitrogen, and air, and plasma treatment for about 1 - 1000 seconds is usually performed with outputs 1-1000W. A reaction start point (not shown) occurs in the front face (a pore internal surface is also included) of the base material 1 put to the plasma at this time.

[0048] Next, the 1st monomer which has an ion exchange group is dissolved in water, and the homogeneity solution of the 1st monomer is prepared. As for the concentration of the water solution of the 1st monomer, it is preferably desirable to carry out to 1 - 10% of the weight 0.1 to 80% of the weight. In addition, the homogeneity solution of the 1st monomer may have the surface active agent, for example, dodecylbenzenesulfonic acid etc., so that this solution may tend to permeate into pore. moreover, the case where the 2nd monomer solution is used for a surfactant -- this -- it may be contained in the 2nd monomer solution.

[0049] The base material 1 after plasma treatment is good to process as follows with the water solution of the 1st monomer of the above. That is, the 1st monomer water solution is made to contact directly under an argon gas ambient atmosphere. Or the point which the base material 1 was made to react with ejection and oxygen, and once carried out activity by the plasma into air is changed into a peroxide radical. Then,

the base material 1 which has a peroxide radical is contacted in the 1st monomer water solution. Contact is performed by more specifically immersing the porous base material 1 which reaction start point has generated in the above-mentioned water solution. In addition, when carrying out directly under an argon gas ambient atmosphere, it is good to perform preferably 20 degrees C - 100 degrees C at the temperature of 30-60 degrees C, and when generating a peroxide radical, it is good [ this process ] to carry [ 60 degrees C - 150 degrees C ] out at 80 degrees C - 120 degrees C preferably. Moreover, immersion is good to carry out carrying out bubbling with inert gas, such as nitrogen gas. As for the immersed time amount, it is good day extent from 1 minute and that it is 1 hour - 24 hours preferably.

[0050] Next, the porous predetermined base material 1 which carried out time amount progress is pulled up from a water solution, and is washed and dried by organic solvents, such as toluene or a xylene. This is for flushing thoroughly the homopolymer secondarily generated in process of the polymerization by the organic solvent, and leaving a graft polymer only to a base material pore front face and the interior.

[0051] Drawing 2 is the perspective view having shown notionally the condition that the monomer carried out graft polymerization in the base material 1. It turns out that the 1st polymer 3 which carried out graft polymerization is formed in the interior not only of the front face of a base material but the pore 2.

[0052] Thus, the base material with which the 1st polymer was formed so that the end might be combined with the pore front face of a porous base material is obtained. Subsequently in this invention, it is filled up with the 2nd polymer in the pore of the obtained base material. As for the 2nd polymer, it is good that it is the polymer which has proton conductivity. That is, as long as it is the 1st above-mentioned polymer and the polymer which has an ion exchange group similarly, even if the same as the 1st polymer, you may differ.

[0053] After the restoration approach of the 2nd polymer is filled up with the approach filled up with the 2nd polymer in direct pore, and the 2nd monomer which serves as the 2nd polymer by subsequent processing in pore, it performs a polymerization reaction within this pore, obtains the 2nd polymer, and has the approach filled up with the 2nd polymer in pore by this.

[0054] When using the 2nd monomer, even if the 2nd monomer is the same as the 1st monomer, it may differ. That is, what chose one sort or two sorts or more from the 1st monomer illustrated above can be used. As the 2nd suitable monomer, what was mentioned above as the 1st monomer is mentioned, and, in addition to this, a vinyl sulfonic acid can be mentioned. In addition, when one sort is chosen as the 2nd monomer, the 2nd polymer is a homopolymer, and the 2nd polymer is a copolymer when two or more sorts are chosen as the 2nd monomer.

[0055] It is desirable the 1st polymer, a chemical bond, and/or that the 2nd polymer is carrying out physical association. For example, the whole of the 2nd polymer may be carrying out the chemical bond to the 1st polymer, or the whole of the 2nd polymer may be carrying out physical association with the 1st polymer. Moreover, a part of 2nd polymer is carrying out the chemical bond to the 1st polymer, and the other 2nd polymers may be carrying out physical association with the 1st polymer. In addition, association with the 1st polymer and the 2nd polymer is mentioned as a chemical bond. This association can be formed, when the reactant radical is made to hold to the 1st polymer and this reactant radical, the 2nd polymer, and/or the 2nd monomer react. Moreover, the condition that the 1st and 2nd polymers become entangled is mentioned as a condition of physical association.

[0056] Proton conductivity can be raised in this invention, without the whole polymer with which it was filled up in pore eluting or flowing out of the inside of pore, controlling transparency (crossover) of a methanol by using together the 1st and 2nd polymers. The whole polymer with which the 1st polymer and 2nd polymer were especially filled up in pore a chemical bond and/or by carrying out physical association does not elute or flow out of the inside of pore. Moreover, even if it is the case that the polymerization degree of the 1st polymer is low, when the 2nd polymer, especially the 2nd polymer with high polymerization degree exist, the proton conductivity of the electrolyte membrane obtained can be raised.

[0057] Hereafter, the restoration approach of the 2nd polymer is briefly explained using drawing 3. Drawing 3 (a) is drawing having shown the cross section of the pore typically about the base material after the 1st polymer was formed. In drawing 3 (a), the same drawing number as drawing 2 is used, pore 2 is formed in the base material 1, and the 1st polymer 3 is formed so that the end may combine with the front face of pore 2.

[0058] Thus, the pore of the base material with which the 1st polymer is formed is filled up with the 2nd monomer, and a polymerization reaction is performed within this pore. It is shown that the 2nd polymer 5 obtained by the polymerization reaction is filled up with drawing 3 (b) in pore. as mentioned above, the 2nd polymer 5 — the 1st polymer 3 and a chemical bond — and/or, physical association is carried out, and the 2nd polymer 5 as well as the 1st polymer is not easily flowed out or eluted out of pore.

[0059] In the electrolyte membrane or the fuel cells, and those manufacture approaches of this invention, the 3rd polymer, the 4th polymer, ..., n-th polymer (namely, n three or more integers) can be used. The n-th polymer may have the operation which raises proton conductivity like the 2nd polymer. Moreover, even if it has the operation which prevents flowing out or eluting the whole polymer from the pore of a base material, the n-th polymer may be constituted so that it may have the other properties needed for a fuel cell.

[0060] As for the electrolyte membrane of this invention, it is desirable to use for the methanol fuel cell containing a fuel cell especially a direct mold methanol solid-state macromolecule fuel cell, or a refining mold methanol solid-state macromolecule fuel cell. As for the electrolyte membrane of this invention, it is desirable especially to use for a direct mold methanol solid-state macromolecule fuel cell.

[0061] Here, the configuration of a methanol fuel cell is explained briefly, referring to drawing 4. Drawing 4 is the schematic diagram showing one mode of the methanol fuel cell which uses the electrolyte membrane of this invention.

[0062] A methanol fuel cell 11 comes to have the electrolyte 17 inserted into the cathode pole 13, the anode pole 15, and these two poles. A methanol fuel cell has the refining machine which is not illustrated in an anode electrode side, and is good also as a refining mold methanol fuel cell.

[0063] It becomes impossible to have the base material layer which can consider a cathode pole as a configuration better known than before, for example, supports a catalyst bed and this catalyst bed sequentially from an electrolyte side. It becomes impossible moreover, to have the base material layer in which an anode electrode can also be considered as a configuration better known than before, for example, supports a catalyst bed and this catalyst bed sequentially from an electrolyte side.

[0064] Furthermore, after really fabricating the 1st pole and electrolyte and acquiring a Plastic solid, the methanol fuel cell which comes to have the electrolyte of this invention can stick this Plastic solid and the 2nd pole, and can also be obtained so that the catalyst bed of the 2nd different pole from the 1st pole and this electrolyte side may stick.

[0065] The case where the 1st pole is a cathode pole is explained using drawing 5. Drawing 5 is the schematic diagram showing one mode of a cathode pole which uses the electrolyte membrane of this invention. The cathode pole 13 comes to have a catalyst bed 21 on the base material layer 19 among drawing 5. As for this base material layer 19, it is desirable to consist of gas permeability and a thing which has oxygen gas permeability, thermal resistance, and electronic conductivity especially. For example, it is good that it is porous carbon and is what has electronic conductivity.

[0066] Moreover, a catalyst bed 21 is a layer which supports a catalyst better known than the former [\*\*\*\*] to the cathode pole. On this catalyst bed 21, the porous thin film 23 which has the pore 2 as shown in drawing 1 is formed. In formation of a porous thin film, the sol used as various glass, such as an alkoxide of various silicon, an alkoxide of various aluminum, an alkoxide of various titanium, or an alkoxide of various zirconiums, or the ceramics is prepared, and this sol is applied to a catalyst bed. An approach better known than before can be used for the applying method for DIP coating, spin coating, spray coating, etc. Thus, the applied sol is warmed by desiccation and request and a porous thin film is obtained. In addition, as for the porous thin film obtained, it is good that it is the thin film of a silica, an alumina (for example, gamma-alumina), a titania, zirconias, these mixtures, or complex.

[0067] In the pore of the obtained porous thin film, by the 1st above-mentioned polymer, for example, a graft polymerization method, or the method of using a coupling agent, the 1st polymer is formed so that the end of this 1st polymer may combine with a pore internal surface. Subsequently, it is filled up with the 2nd polymer in pore by the above-mentioned approach. Thus, a cathode pole and an electrolyte can really fabricate. Such by really using a Plastic solid, handling of the thin-film-ized electrolyte membrane becomes easy.

[0068] Adhesion shaping can be carried out and a methanol fuel cell can be formed so that the electrolyte side of a Plastic solid may stick this Plastic solid and an anode pole the catalyst bed side of an anode pole. In addition, in \*\*\*\*, although how to really fabricate a cathode pole and an electrolyte was described, if it is also this contractor to really fabricate an anode pole and an electrolyte, it can hit on an idea easily from \*\*\*\*.

[0069] [Example] Although this invention is explained in more detail based on an example, this invention is not limited to this example.

(Example 1) The porous PTFE film (70 micrometers in trademark Teflon, the NITTO DENKO make, a flat film, and thickness, 50nm of pore size) was used as a base material. The base material concerned was washed and the plasma exposure was performed on condition that the following.

[0070] RF output: 30W;  
 Plasma irradiation time: For 60 sec;  
 Ambient atmosphere: Argon gas;  
 Pressure: 10Pa.

[0071] It was immersed in the 1st monomer solution which carried out freezing deaeration of the base material after a plasma exposure, and graft polymerization was performed. Graft polymerization conditions are shown below.

[0072] Monomer: Acrylic acid (AA);  
 Monomer concentration: 10 % of the weight;  
 Solvent: Water;  
 Temperature: About 60 degrees C;

time amount: — 10 - 24 hour; and additive: — a surface active agent (sodium dodecylbenzenesulfonate).

[0073] After pulling up the porous base material from the solution and washing it underwater, the film A-1 which was dried and formed the 1st polymer was obtained. The mass of the film A-1 was measured after desiccation, and the amount of graft polymerization was calculated as compared with the mass before a polymerization. The amount of graft polymerization was 0.7 mg/cm<sup>2</sup>. Incidentally, the film pressure after a polymerization was about 90 micrometers.

[0074] In this way, when FT-IR (Mapping law) measurement of the obtained film A-1 was carried out, it was checked that the peak of 1740cm<sup>-1</sup> of a carboxyl group exists also inside membranous, and it became clear that the polymer was formed also in the interior of membranous.

[0075] It <restoration of the 2nd polymer> Ranked second and was filled up with the 2nd polymer. The acrylic acid (AA) was used like the 1st polymer as the 2nd monomer. The 2nd monomer 98.9 weight section and the 2nd monomer solution which consists of the divinylbenzene 0.1 weight section and the water-soluble azo system polymerization initiator 1.0 weight section as a cross linking agent were prepared. The film A-1 obtained above was immersed in this 2nd polymer solution.

[0076] The light was irradiated for 6 minutes after immersion, and the thermal polymerization reaction was made to perform inside pore. Then, the film A-2 which backwashing by water of the obtained film is carried out in a supersonic wave, and it dried and was made to fill up with the 1st and 2nd polymers was obtained. In addition, the difference of the weight before and behind restoration of the 2nd polymer showed that 7.0mg /of laps was [ cm ] 2.

[0077] (Example 2) In order to consider as the 2nd monomer and to dissolve a vinyl sulfonic acid, using the mixture of acrylic-acid (AA):vinyl sulfonic-acid =2:1, the film A-3 was obtained by the same approach as an example 1 except having used the water of an amount a little.

[0078] (Example 1 of reference) The film A-4 filled up only with the 1st polymer as well as the film A-1 of an example 1 was obtained. However, the lap of the film A-4 was 3.0 mg/cm<sup>2</sup>.

[0079] <Proton conductivity measurement> The proton conductivity was measured about the obtained film A-2 to A-4. On the occasion of measurement, the film was made to swell underwater, it inserted into the stainless steel foil electrode after that first, and the proton conductivity test sample was produced. About these samples, impedance measurement was performed by HP4192made from Hewlett Packard A. The obtained result is shown below.

[0080] Film A-4(example 1 of reference):0.04x10<sup>-2</sup> S/cm;  
 Film A-2(example 1):0.10x10<sup>-2</sup> S/cm; and film A-3(example 2):0.62x10<sup>-2</sup> S/cm.

[0081] Thus, high proton conductivity was able to be acquired by being filled up with the 2nd polymer. In addition, each of film A-2 and A-3 had desired thermal resistance and the methanol inhibition engine performance. That is, it turned out that the electrolyte membrane A-2 of this example and A-3 have the low permeability of a methanol, and heat-resistant and high proton conductivity.

[0082]  
 [Effect of the Invention] The new electrolyte membrane which controls transparency (crossover) of a methanol as much as possible, and is equal also to the activity under an elevated-temperature (about 130 degrees C or more) environment with this invention can be offered. moreover, this invention — everything but the above-mentioned effectiveness — or the above-mentioned effectiveness — in addition, although the approach of manufacturing the above-mentioned electrolyte membrane is offered, it can do. furthermore, this invention — everything but the above-mentioned effectiveness — or the above-mentioned effectiveness — in addition, the new methanol direct mold solid-state macromolecule fuel cell using the above-mentioned electrolyte membrane can be offered.

[Translation done.]





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TECHNICAL FIELD

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[Field of the Invention] Generally, about an electrolyte membrane, it is related with a detail at the electrolyte membrane for fuel cells, and a pan, and this invention relates to a detail at the electrolyte membrane for direct mold methanol polymer electrolyte fuel cells. Moreover, this invention relates to the fuel cell which comes to have this electrolyte membrane, and its manufacture approach.

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PRIOR ART

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[Description of the Prior Art] The so-called blowdown prevention of greenhouse gases and NO<sub>x</sub> is strongly cried for as the movement toward terrestrial environmental protection activates. In order to reduce the total emission of these gas, utilization of the fuel cell system for automobiles is considered to be very effective.

[0003] The polymer electrolyte fuel cell (PEFC, Polymer Electrolyte Fuel Cell) has the outstanding description that only water is generated at low-temperature actuation, high power density, and a generation-of-electrical-energy reaction. In as well as [ a gasoline ], since it can supply as liquid fuel, it is thought that PEFC of a methanol fuel is promising as power for electric vehicles.

[0004] A polymer electrolyte fuel cell is classified into two types, the refining mold which changes a methanol into the gas of a hydrogen principal component using a refining machine, and the direct mold (DMFC, Direct Methanol Polymer Fuel Cell) which uses a methanol directly, without using a refining machine. A direct mold fuel cell has the big advantage of that the load-effect responsibility which can be equal to frequent starting and halt possible [ lightweight-izing ] is also substantially improvable since the refining machine is unnecessary, catalyst poisoning not becoming a problem, either, and the utilization is expected.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The new electrolyte membrane which controls transparency (crossover) of a methanol as much as possible, and is equal also to the activity under an elevated-temperature (about 130 degrees C or more) environment with this invention can be offered. moreover, this invention -- everything but the above-mentioned effectiveness -- or the above-mentioned effectiveness -- in addition, although the approach of manufacturing the above-mentioned electrolyte membrane is offered, it can do. furthermore, this invention -- everything but the above-mentioned effectiveness -- or the above-mentioned effectiveness -- in addition, the new methanol direct mold solid-state macromolecule fuel cell using the above-mentioned electrolyte membrane can be offered.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, some troubles are pointed out to utilization of DMFC. For example, although DMFC uses a solid-state polyelectrolyte as an electrolyte When the electrolyte membrane for ordinary PEFC, for example, the Nafion (trademark) film of Du Pont, the Dow film of Dow Chemical, etc. are used Two big problems of the problem of dissolving near 130 degree C if temperature is raised in order to raise the problem that a catalyst carries out depolarization and electromotive force declines in order that a methanol may penetrate the film, and catalytic activity (creeping) occur. Although the electrolyte membrane which solves these problems simultaneously is not existing, if this problem is solved, the application to an electric vehicle may progress at a stretch.

[0006] Therefore, the object of this invention is to realize the new electrolyte membrane which controls transparency (crossover) of a methanol as much as possible, and is equal also to the activity under an elevated-temperature (about 130 degrees C or more) environment. Moreover, the object of this invention is to offer the manufacture approach of the above-mentioned electrolyte membrane. Furthermore, the object of this invention is to realize the new methanol direct mold solid-state macromolecule fuel cell which used the above-mentioned electrolyte membrane.

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MEANS

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[Means for Solving the Problem] In order to solve the above-mentioned trouble, this invention persons acquired the following knowledge, as a result of repeating examination wholeheartedly. That is, generally, although the polymer was softened at the elevated temperature, when the temperature to pyrolyze carried out the chemical bond of the 1st polymer and embedded it into the pore of a heat-resistant base material paying attention to the property to maintain the engine performance, the knowledge that the frame of a base material maintained membranous structure also under an elevated temperature was acquired.

[0008] Moreover, this invention persons acquired the knowledge that proton conductivity could be raised, controlling transparency (crossover) of a methanol, when you made it filled up with the 2nd polymer in addition to the 1st polymer. Furthermore, while securing proton conductivity by the polymer embedded into pore, the configuration maintenance under an elevated temperature, swelling control, and thermal resistance acquired the knowledge that the matrix of a porous base material could attain.

[0009] From these knowledge, this invention persons found out the following invention.

<1> The manufacture approach of an electrolyte membrane that are the manufacture approach of an electrolyte membrane of having the process which makes it filled up with the 2nd polymer which may differ even if the same as the process which forms the 1st polymer, and the 1st polymer so that the end may be combined with the pore internal surface of a porous base material which has bloating tendency-proof in an organic solvent and water in the pore of said base material, and said 1st and 2nd polymers have proton conductivity.

[0010] <2> In the above <1>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<3> In the above <1> or <2>, it is good to form the 1st polymer so that the end may be combined with the pore internal surface of a base material by having the process to which the formation process of the 1st polymer irradiates energy at a base material, and the process which contacts the 1st monomer to this base material, and contacting the 1st monomer.

[0011] <4> In the above <3>, it is good to form the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<5> In the above <1> or <2>, it is good for the formation process of the 1st polymer to combine the end of the 1st polymer with a base material by the coupling agent.

[0012] <6> In either of above-mentioned <1>- <5>, it is good that it is the process which the polymerization of the 2nd monomer with which the restoration process of the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material is carried out into pore, and the 2nd polymer is obtained, and is made by this to fill up with the inside of pore.

<7> In either of above-mentioned <1>- <6>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

<8> As for an inorganic material, in the above <7>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

[0013] <9> In the above <7>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<10> In either of above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

<11> In either of above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte

membrane for direct mold methanol solid-state macromolecule fuel cells.

[0014] <12> It is the electrolyte membrane characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity. The electrolyte membrane which this polymer has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer is a polymer which combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[0015] <13> In the above <12>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<14> In the above <12> or <13>, after the 1st polymer irradiates energy at a base material, it is good to be obtained by contacting the 1st monomer to this base material.

[0016] <15> In the above <14>, it is good to obtain the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with said base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<16> In the above <12> or <13>, the 1st polymer is good to combine the end with a base material by the coupling agent.

[0017] <17> In either of above-mentioned <12>- <16>, it is good to carry out the polymerization of the 2nd monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore, and to be obtained.

[0018] <18> In either of above-mentioned <12>- <17>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

<19> As for an inorganic material, in the above <18>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

[0019] <20> In the above <18>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<21> In either of above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

<22> In either of above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for direct mold methanol solid-state macromolecule fuel cells.

[0020] <23> Fuel cell this whose electrolyte membrane it is the fuel cell in which the electrolyte membrane was formed on the cathode electrode or the catalyst bed of a cathode electrode, and is one electrolyte membrane of above-mentioned <12>- <22>.

[0021] <24> It is the fuel cell which comes to have the electrolyte inserted into a cathode pole, an anode pole, and these two poles. This electrolyte It is the electrolyte characterized by filling up the pore of the porous base material which is not substantially swollen to a methanol and water with the polymer which has proton conductivity. The fuel cell which this polymer is a polymer to which it has the 1st proton conductivity polymer and the 2nd proton conductivity polymer, and this 1st polymer combined the end with the pore internal surface of said base material, and is the polymer from which the 2nd polymer may be the same as the 1st polymer, or may differ.

[0022] <25> In the above <24>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

<26> In the above <24> or <25>, after the 1st polymer irradiates energy at a base material, it is good to be obtained by contacting the 1st monomer to this base material.

[0023] <27> In the above <26>, it is good to obtain the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<28> In the above <24> or <25>, the 1st polymer is good to combine the end with a base material by the coupling agent.

[0024] <29> In either of above-mentioned <24>- <28>, it is good to carry out the polymerization of the 2nd monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore, and to be obtained.

<30> In either of above-mentioned <24>- <29>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

[0025] <31> As for an inorganic material, in the above <30>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

<32> In the above <30>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

<33> In either of above-mentioned <24>- <32>, it is good that a fuel cell is a direct mold methanol solid-state macromolecule fuel cell.

[0026] <34> The process which applies a sol to the 1st pole, the process which uses the applied sol as a porous thin film layer, The process which fills up the pore of the obtained porous thin film layer with a proton conductivity polymer, and forms an electrolyte membrane on the 1st electrode, In the process which is the manufacture approach of a fuel cell of having the process at which the 2nd pole is stuck, and forms said electrolyte membrane on this electrolyte membrane Said proton conductivity polymer has the 1st and 2nd proton conductivity polymers. The manufacture approach of a fuel cell of having the process which forms this 1st polymer so that the end of this 1st polymer may combine with the front face of said pore, and the process filled up with the 2nd polymer after formation of the 1st polymer.

[0027] <35> In the above <34>, the 1st polymer and 2nd polymer may be the same, or may differ from each other.

<36> In the above <34> or <35>, the 1st polymer is the 1st monomer origin and it is good that it is the 2nd monomer origin from which the 2nd polymer may be the same as the 1st monomer, or may differ.

[0028] <37> In either of above-mentioned <34>- <36>, after the formation process of the 1st polymer irradiates energy at a base material, it is good to be carried out by contacting the 1st monomer to this base material.

[0029] <38> In the above <37>, it is good to obtain the 1st polymer so that it may be chosen out of the group which the energy source of energy becomes from the plasma, ultraviolet rays, an electron ray, and a gamma ray, a base material may be excited by this energy source and it may combine with a base material in this reaction start point by [ of this base material ] generating a reaction start point to a pore internal surface at least, and contacting the 1st monomer to this reaction start point.

<39> In either of above-mentioned <34>- <36>, it is good for the formation process of the 1st polymer to combine the end of the 1st polymer with a base material by the coupling agent.

[0030] <40> In either of above-mentioned <34>- <39>, it is good to be obtained by carrying out the polymerization of the 2nd monomer with which the 2nd polymer filled up with and this filled up the 2nd monomer in the pore of a base material into pore.

<41> In either of above-mentioned <34>- <40>, a porous base material is good to consist of an inorganic material or a heat-resistant polymer.

[0031] <42> As for an inorganic material, in the above <41>, it is good that they are any one or those composite material of a ceramic, glass, or an alumina.

<43> In the above <41>, it is good that a heat-resistant polymer is polytetrafluoroethylene or polyimide.

[0032] <44> In either of above-mentioned <34>- <43>, it is good for the 1st pole to come to have the 1st base material layer and 1st catalyst bed, and to apply said sol to said catalyst bed in a sol spreading process.

<45> In either of above-mentioned <34>- <44>, it is good to stick said electrolyte membrane and said 2nd catalyst bed in the process at which the 2nd pole comes to have the 2nd base material layer and 2nd catalyst bed, and sticks the 2nd pole.

[0033] <46> In either of above-mentioned <34>- <45>, it is good that a fuel cell is a direct mold methanol solid-state macromolecule fuel cell.

[0034]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The electrolyte membrane of this invention has thermal resistance, and the foam which is not substantially swollen to an organic solvent and water, such as a methanol, is used for it as a base material. As an ingredient with such a property, there is ceramics, such as glass, an alumina, or a silica, etc. with an inorganic material. Moreover, with other ingredients, polytetrafluoroethylene (for example, Teflon (trademark)), polyimide, etc. are mentioned. These ingredients may be used independently or two or more sorts may be used for them as a composite material. Moreover, when using as a composite material, more than two-layer may come to carry out the laminating of the gestalt.

[0035] As for the void content of the base material which can be used for this invention, it is suitably good that it is 10% - 95%. Moreover, as for an average aperture, it is desirable that it is within the limits of 0.001 micrometers - 100 micrometers. Furthermore, as for the thickness of a base material, it is preferably good that it is [ 100 micrometers or less ] several micrometers order.

[0036] The electrolyte membrane of this invention comes to combine the 1st polymer, especially a graft

polymer with the front face, especially pore internal surface of the base material which consists of foam. This 1st polymer is the 1st monomer origin, and the 1st monomer and 1st polymer have an ion exchange group. This 1st polymer, especially a graft polymer fill the inside of the pore of a base material first. Since the 1st polymer is formed so that the end may combine with a pore internal surface, this 1st polymer formed in pore is not flowed out or eluted easily.

[0037] In addition, in this description, an "ion exchange group" means the radical which  $\text{-SO}_3\text{-}$  or for example, the  $\text{-SO}_3\text{H}$  set origin etc. holds a proton, and is easy to separate. When these exist in the 1st polymer in the shape of a pendant and this polymer fills the inside of pore, proton conductivity arises.

[0038] In order to form the 1st polymer so that the end may be combined with a pore internal surface, there are the following approaches. For example, a base material is excited by the plasma, ultraviolet rays, the electron ray, a gamma ray, etc., and it is the approach of obtaining the 1st polymer, by [ of this base material ] making a pore internal surface generate a reaction start point at least, and contacting the 1st monomer to this reaction start point. Moreover, the 1st polymer can also be combined with a pore internal surface by the chemical approach of a silane coupler etc. Furthermore, it is filled up with the 1st monomer into pore, and after using the general polymerization method for making a polymerization reaction perform in the interior, and obtaining the 1st polymer, the chemical bond of the 1st obtained polymer can be carried out to a base material using the coupling agent containing for example, the above-mentioned silane coupler etc.

[0039] In this invention, it is desirable to use the plasma graft polymerization method explained below. That is, it is desirable to obtain the 1st polymer which was made to carry out the plasma graft polymerization reaction of the 1st monomer, and the end combined with the pore front face. In addition, plasma graft polymerization can be performed using the liquid phase process explained below and a well-known vapor-phase-polymerization method.

[0040] As for a monomer usable as the 1st monomer of this invention, acrylic sulfonic-acid sodium (SAS), sodium methallylsulfonate (SMS), p styrene sulfonic-acid sodium (SSS), an acrylic acid (AA), etc. are mentioned suitably. However, a monomer usable to this invention Not the thing limited above but allylamine, an allyl compound sulfonic acid, Allyl compound phosphonic acid, a metallyl sulfonic acid, metallyl phosphonic acid, a vinyl sulfonic acid, Vinyl phosphonic acid, a styrene sulfonic acid, styrene phosphonic acid, the sulfonic acid of acrylamide, or a phosphonic acid derivative, Ethyleneimine, methacrylic acids, etc. may be derivatives, such as a monomer which has weak acid radicals, such as strong acid radicals, such as a vinyl group and a sulfonic acid, and phosphonic acid, and a carboxyl group, the 1st class, the 2nd class, the 3rd class, a strong base like the 4th class amine, and a weak base in structure, and its ester. In addition, when the type of salts, such as sodium salt, is used as a monomer, after considering as a polymer, it is good to use those salts as a proton mold etc.

[0041] Moreover, one sort of homopolymers may be formed using these monomers, two or more sorts may be used and a copolymer may be formed. That is, the 1st polymer which the end combined with the front face in the pore of a base material may be a homopolymer, or may be a copolymer.

[0042] The proton conductivity of an electrolyte membrane changes depending on the class of the 1st monomer to be used and/or the 2nd monomer mentioned later. Therefore, it is desirable to use a monomer ingredient with high proton conductivity. Moreover, it depends for electrolytic proton conductivity also on the polymerization degree of the polymer which fills the inside of pore.

[0043] In addition, in this invention, proton conductivity is given by being formed and/or filled up with the 1st polymer and the 2nd polymer mentioned later in pore. Therefore, it is good for the 1st polymer and 2nd polymer to have polymerization degree with high both sides, or to crawl, and for a gap or one side to have high polymerization degree. It is good for the 2nd polymer to have high polymerization degree on manufacture effectiveness especially. Or although both sides do not have high polymerization degree relatively, it is good by combining both sides for each to have the polymerization degree of extent which has high proton conductivity.

[0044] After a plasma graft polymerization method usable to manufacture of the electrolyte membrane of this invention irradiates the plasma at a base material and makes a base material front face and a pore internal surface generate a reaction start point, it is suitably contacted by the approach of the liquid phase polymerization common knowledge of the 1st monomer, and carries out the graft polymerization of the 1st monomer in the interior of a base material front face and pore.

[0045] It explains in detail, referring to a drawing about an usable plasma graft polymerization method to this invention next. The detailed content of the plasma graft polymerization method is explained also to the precedence application by the artificers of this invention, JP,3-98632,A, JP,4-334531,A, JP,5-31343,A, JP,5-237352,A, and JP,6-246141,A in detail.



[0046] Drawing 1 is the partial cross-section perspective view having shown the usable porous base material 1 in the electrolyte membrane of this invention. To the porous base material 1, the pore 2 which penetrates a base material is opening many.

[0047] The frequency of 10–50MHz is performed to the porous base material 1 under existence of gas, such as an argon with which a pressure range serves as 120kPa(s) from 1mPa, nitrogen, and air, and plasma treatment for about 1 – 1000 seconds is usually performed with outputs 1–1000W. A reaction start point (not shown) occurs in the front face (a pore internal surface is also included) of the base material 1 put to the plasma at this time.

[0048] Next, the 1st monomer which has an ion exchange group is dissolved in water, and the homogeneity solution of the 1st monomer is prepared. As for the concentration of the water solution of the 1st monomer, it is preferably desirable to carry out to 1 – 10% of the weight 0.1 to 80% of the weight. In addition, the homogeneity solution of the 1st monomer may have the surface active agent, for example, dodecylbenzenesulfonic acid etc., so that this solution may tend to permeate into pore. moreover, the case where the 2nd monomer solution is used for a surfactant — this — it may be contained in the 2nd monomer solution.

[0049] The base material 1 after plasma treatment is good to process as follows with the water solution of the 1st monomer of the above. That is, the 1st monomer water solution is made to contact directly under an argon gas ambient atmosphere. Or the point which the base material 1 was made to react with ejection and oxygen, and once carried out activity by the plasma into air is changed into a peroxide radical. Then, the base material 1 which has a peroxide radical is contacted in the 1st monomer water solution. Contact is performed by more specifically immersing the porous base material 1 which the reaction start point has generated in the above-mentioned water solution. In addition, when carrying out directly under an argon gas ambient atmosphere, it is good to perform preferably 20 degrees C – 100 degrees C at the temperature of 30–60 degrees C, and when generating a peroxide radical, it is good [ this process ] to carry [ 60 degrees C – 150 degrees C ] out at 80 degrees C – 120 degrees C preferably. Moreover, immersion is good to carry out carrying out bubbling with inert gas, such as nitrogen gas. As for the immersed time amount, it is good day extent from 1 minute and that it is 1 hour – 24 hours preferably.

[0050] Next, the porous predetermined base material 1 which carried out time amount progress is pulled up from a water solution, and is washed and dried by organic solvents, such as toluene or a xylene. This is for flushing thoroughly the homopolymer secondarily generated in process of the polymerization by the organic solvent, and leaving a graft polymer only to a base material pore front face and the interior.

[0051] Drawing 2 is the perspective view having shown notionally the condition that the monomer carried out graft polymerization in the base material 1. It turns out that the 1st polymer 3 which carried out graft polymerization is formed in the interior not only of the front face of a base material but the pore 2.

[0052] Thus, the base material with which the 1st polymer was formed so that the end might be combined with the pore front face of a porous base material is obtained. Subsequently in this invention, it is filled up with the 2nd polymer in the pore of the obtained base material. As for the 2nd polymer, it is good that it is the polymer which has proton conductivity. That is, as long as it is the 1st above-mentioned polymer and the polymer which has an ion exchange group similarly, even if the same as the 1st polymer, you may differ.

[0053] After the restoration approach of the 2nd polymer is filled up with the approach filled up with the 2nd polymer in direct pore, and the 2nd monomer which serves as the 2nd polymer by subsequent processing in pore, it performs a polymerization reaction within this pore, obtains the 2nd polymer, and has the approach filled up with the 2nd polymer in pore by this.

[0054] When using the 2nd monomer, even if the 2nd monomer is the same as the 1st monomer, it may differ. That is, what chose one sort or two sorts or more from the 1st monomer illustrated above can be used. As the 2nd suitable monomer, what was mentioned above as the 1st monomer is mentioned, and, in addition to this, a vinyl sulfonic acid can be mentioned. In addition, when one sort is chosen as the 2nd monomer, the 2nd polymer is a homopolymer, and the 2nd polymer is a copolymer when two or more sorts are chosen as the 2nd monomer.

[0055] It is desirable the 1st polymer, a chemical bond, and/or that the 2nd polymer is carrying out physical association. For example, the whole of the 2nd polymer may be carrying out the chemical bond to the 1st polymer, or the whole of the 2nd polymer may be carrying out physical association with the 1st polymer. Moreover, a part of 2nd polymer is carrying out the chemical bond to the 1st polymer, and the other 2nd polymers may be carrying out physical association with the 1st polymer. In addition, association with the 1st polymer and the 2nd polymer is mentioned as a chemical bond. This association can be formed, when the reactant radical is made to hold to the 1st polymer and this reactant radical, the 2nd

polymer, and/or the 2nd monomer react. Moreover, the condition that the 1st and 2nd polymers become entangled is mentioned as a condition of physical association.

[0056] Proton conductivity can be raised in this invention, without the whole polymer with which it was filled up in pore eluting or flowing out of the inside of pore, controlling transparency (crossover) of a methanol by using together the 1st and 2nd polymers. The whole polymer with which the 1st polymer and 2nd polymer were especially filled up in pore a chemical bond and/or by carrying out physical association does not elute or flow out of the inside of pore. Moreover, even if it is the case that the polymerization degree of the 1st polymer is low, when the 2nd polymer, especially the 2nd polymer with high polymerization degree exist, the proton conductivity of the electrolyte membrane obtained can be raised.

[0057] Hereafter, the restoration approach of the 2nd polymer is briefly explained using drawing 3. Drawing 3 (a) is drawing having shown the cross section of the pore typically about the base material after the 1st polymer was formed. In drawing 3 (a), the same drawing number as drawing 2 is used, pore 2 is formed in the base material 1, and the 1st polymer 3 is formed so that the end may combine with the front face of pore 2.

[0058] Thus, the pore of the base material with which the 1st polymer is formed is filled up with the 2nd monomer, and a polymerization reaction is performed within this pore. It is shown that the 2nd polymer 5 obtained by the polymerization reaction is filled up with drawing 3 (b) in pore. as mentioned above, the 2nd polymer 5 — the 1st polymer 3 and a chemical bond — and/or, physical association is carried out, and the 2nd polymer 5 as well as the 1st polymer is not easily flowed out or eluted out of pore.

[0059] In the electrolyte membrane or the fuel cells, and those manufacture approaches of this invention, the 3rd polymer, the 4th polymer, ..., the n-th polymer (namely, n three or more integers) can be used. The n-th polymer may have the operation which raises proton conductivity like the 2nd polymer. Moreover, even if it has the operation which prevents flowing out or eluting the whole polymer from the pore of a base material, the n-th polymer may be constituted so that it may have the other properties needed for a fuel cell.

[0060] As for the electrolyte membrane of this invention, it is desirable to use for the methanol fuel cell containing a fuel cell especially a direct mold methanol solid-state macromolecule fuel cell, or a refining mold methanol solid-state macromolecule fuel cell. As for the electrolyte membrane of this invention, it is desirable especially to use for a direct mold methanol solid-state macromolecule fuel cell.

[0061] Here, the configuration of a methanol fuel cell is explained briefly, referring to drawing 4. Drawing 4 is the schematic diagram showing one mode of the methanol fuel cell which uses the electrolyte membrane of this invention.

[0062] A methanol fuel cell 11 comes to have the electrolyte 17 inserted into the cathode pole 13, the anode pole 15, and these two poles. A methanol fuel cell has the refining machine which is not illustrated in an anode electrode side, and is good also as a refining mold methanol fuel cell.

[0063] It becomes impossible to have the base material layer which can consider a cathode pole as a configuration better known than before, for example, supports a catalyst bed and this catalyst bed sequentially from an electrolyte side. It becomes impossible moreover, to have the base material layer in which an anode electrode can also be considered as a configuration better known than before, for example, supports a catalyst bed and this catalyst bed sequentially from an electrolyte side.

[0064] Furthermore, after really fabricating the 1st pole and electrolyte and acquiring a Plastic solid, the methanol fuel cell which comes to have the electrolyte of this invention can stick this Plastic solid and the 2nd pole, and can also be obtained so that the catalyst bed of the 2nd different pole from the 1st pole and this electrolyte side may stick.

[0065] The case where the 1st pole is a cathode pole is explained using drawing 5. Drawing 5 is the schematic diagram showing one mode of a cathode pole which uses the electrolyte membrane of this invention. The cathode pole 13 comes to have a catalyst bed 21 on the base material layer 19 among drawing 5. As for this base material layer 19, it is desirable to consist of gas permeability and a thing which has oxygen gas permeability, thermal resistance, and electronic conductivity especially. For example, it is good that it is porous carbon and is what has electronic conductivity.

[0066] Moreover, a catalyst bed 21 is a layer which supports a catalyst better known than the former [\*\*\*\*] to the cathode pole. On this catalyst bed 21, the porous thin film 23 which has the pore 2 as shown in drawing 1 is formed. In formation of a porous thin film, the sol used as various glass, such as an alkoxide of various silicon, an alkoxide of various aluminum, an alkoxide of various titanium, or an alkoxide of various zirconiums, or the ceramics is prepared, and this sol is applied to a catalyst bed. An approach better known than before can be used for the applying method for DIP coating, spin coating, spray coating, etc. Thus, the applied sol is warmed by desiccation and request and a porous thin film is obtained. In

addition, as for the porous thin film obtained, it is good that it is the thin film of a silica, an alumina (for example, gamma-alumina), a titania, zirconias, these mixtures, or complex.

[0067] In the pore of the obtained porous thin film, by the 1st above-mentioned polymer, for example, a graft polymerization method, or the method of using a coupling agent, the 1st polymer is formed so that the end of this 1st polymer may combine with a pore internal surface. Subsequently, it is filled up with the 2nd polymer in pore by the above-mentioned approach. Thus, a cathode pole and an electrolyte can really fabricate. Such by really using a Plastic solid, handling of the thin-film-ized electrolyte membrane becomes easy.

[0068] Adhesion shaping can be carried out and a methanol fuel cell can be formed so that the electrolyte side of a Plastic solid may stick this Plastic solid and an anode pole the catalyst bed side of an anode pole. In addition, in \*\*\*\*, although how to really fabricate a cathode pole and an electrolyte was described, if it is also this contractor to really fabricate an anode pole and an electrolyte, it can hit on an idea easily from \*\*\*\*.

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EXAMPLE

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[Example] Although this invention is explained in more detail based on an example, this invention is not limited to this example.

(Example 1) The porous PTFE film (70 micrometers in trademark Teflon, the NITTO DENKO make, a flat film, and thickness, 50nm of pore size) was used as a base material. The base material concerned was washed and the plasma exposure was performed on condition that the following.

[0070] RF output: 30W;

Plasma irradiation time: For 60 seconds;

Ambient atmosphere: Argon gas;

Pressure: 10Pa.

[0071] It was immersed in the 1st monomer solution which carried out freezing deaeration of the base material after a plasma exposure, and graft polymerization was performed. Graft polymerization conditions are shown below.

[0072] Monomer: Acrylic acid (AA);

Monomer concentration: 10 % of the weight;

Solvent: Water;

Temperature: About 60 degrees C;

time amount: — 10 – 24 hour; and additive: — a surface active agent (sodium dodecylbenzenesulfonate).

[0073] After pulling up the porous base material from the solution and washing it underwater, the film A-1 which was dried and formed the 1st polymer was obtained. The mass of the film A-1 was measured after desiccation, and the amount of graft polymerization was calculated as compared with the mass before a polymerization. The amount of graft polymerization was 0.7 mg/cm<sup>2</sup>. Incidentally, the film pressure after a polymerization was about 90 micrometers.

[0074] In this way, when FT-IR (Mapping law) measurement of the obtained film A-1 was carried out, it was checked that the peak of 1740cm<sup>-1</sup> of a carboxyl group exists also inside membranous, and it became clear that the polymer was formed also in the interior of membranous.

[0075] It <restoration of the 2nd polymer> Ranked second and was filled up with the 2nd polymer. The acrylic acid (AA) was used like the 1st polymer as the 2nd monomer. The 2nd monomer 98.9 weight section and the 2nd monomer solution which consists of the divinylbenzene 0.1 weight section and the water-soluble azo system polymerization initiator 1.0 weight section as a cross linking agent were prepared. The film A-1 obtained above was immersed in this 2nd polymer solution.

[0076] The light was irradiated for 6 minutes after immersion, and the thermal polymerization reaction was made to perform inside pore. Then, the film A-2 which backwashing by water of the obtained film is carried out in a supersonic wave, and it dried and was made to fill up with the 1st and 2nd polymers was obtained. In addition, the difference of the weight before and behind restoration of the 2nd polymer showed that 7.0mg / of laps was [ cm ] 2.

[0077] (Example 2) In order to consider as the 2nd monomer and to dissolve a vinyl sulfonic acid, using the mixture of acrylic-acid (AA):vinyl sulfonic-acid =2:1, the film A-3 was obtained by the same approach as an example 1 except having used the water of an amount a little.

[0078] (Example 1 of reference) The film A-4 filled up only with the 1st polymer as well as the film A-1 of an example 1 was obtained. However, the lap of the film A-4 was 3.0 mg/cm<sup>2</sup>.

[0079] <Proton conductivity measurement> The proton conductivity was measured about the obtained film A-2 to A-4. On the occasion of measurement, the film was made to swell underwater, it inserted into the stainless steel foil electrode after that first, and the proton conductivity test sample was produced. About these samples, impedance measurement was performed by HP4192made from Hewlett Packard A. The

obtained result is shown below.

[0080] Film A-4(example 1 of reference 1): $0.04 \times 10^{-2}$  S/cm;

Film A-2(example 1): $0.10 \times 10^{-2}$  S/cm, and film A-3(example 2): $0.62 \times 10^{-2}$  S/cm.

[0081] Thus, high proton conductivity was able to be acquired by being filled up with the 2nd polymer. In addition, each of film A-2 and A-3 had desired thermal resistance and the methanol inhibition engine performance. That is, it turned out that the electrolyte membrane A-2 of this example and A-3 have the low permeability of a methanol, and heat-resistant and high proton conductivity.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram of the porous base material used for this invention.

[Drawing 2] It is the mimetic diagram showing having formed the 1st monomer in the pore of the porous base material used for this invention.

[Drawing 3] It is the mimetic diagram filled up with the 2nd polymer of this invention.

[Drawing 4] It is the schematic diagram showing one mode of the methanol fuel cell using the electrolyte membrane of this invention.

[Drawing 5] It is the schematic diagram showing one mode of the cathode electrode using the electrolyte membrane of this invention.

[Description of Notations]

1 Porous Base Material, 2 Pore, 3 1st Polymer, 5 2nd Polymer, 11 Methanol Fuel Cell, 13 Cathode Pole, 15 Anode Pole, 17 Electrolyte, 19 Base Material Layer, 21 Catalyst Bed, 23 Porous Thin Film

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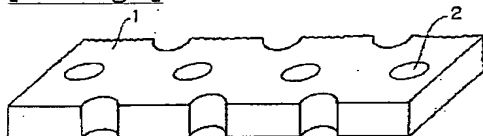
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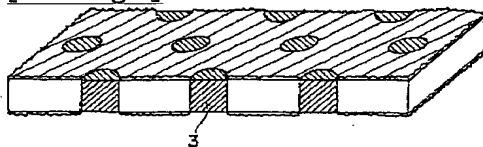
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## DRAWINGS

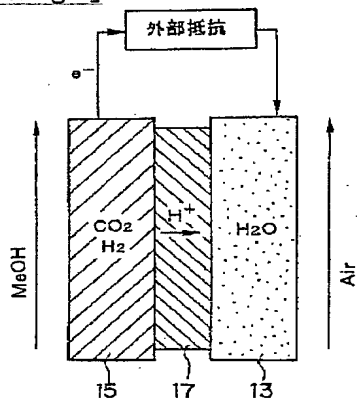
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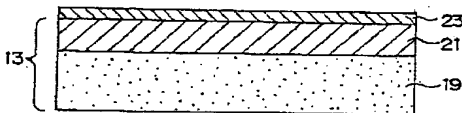
[Drawing 2]



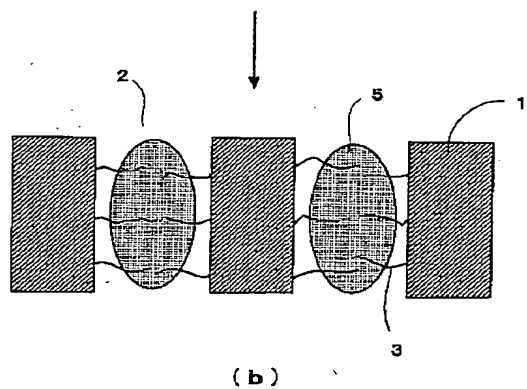
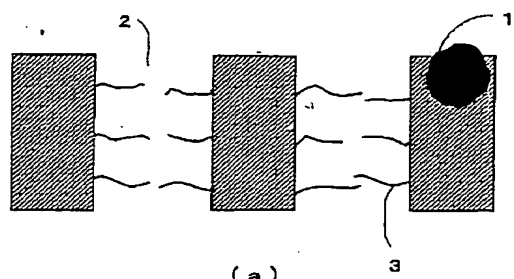
[Drawing 4]



[Drawing 5]



[Drawing 3]



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